Evaluering og udvikling af metoder til prøvetagning og feltanalyse af anoxisk grundvand

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EVALUERING OG UDVIKLING AF METODER TIL PRØVETAGNING OG FELTANALYSE AF ANOXISK GRUNDVAND

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SAMMENFATNING

Projektet omhandler udvikling og evaluering af metoder til prøvetagning og feltanalyse af grundvandsprøver med særlig vægt på redox-følsomme parametre.

Første del omfatter en beskrivelse og afprøvning af en nyudviklet multisampler til dybde-specifik prøvetagning af grundvand uden at prøverne kommer i kontakt med atmosfæren. Multisampleren består af et ydre rør med indbyggede prøvetagere for hver meter. Prøven opsamles v.h.a. N_2-tryk i et lukket system. Yderligere beskrives et trykfiltrerings udstyr som monteres direkte på prøvetagerne og som muliggør anoxisk filtrering af prøverne. Udstyret er blevet afprøvet i Rabis Bæk-området i sandede hedesletteaflejringer. Resultaterne viser at skarpe redoxgrænser i magasinet kan registreres og reproduceres. Desuden demonstreres der en god sammenhæng imellem variationer i grundvandskemien og sedimentkemiske data.

I rapportens anden del gennemgås problemerne omkring pH-måling i svag bufferede grundvandsprøver. Det vises at feltmålinger er absolut nødvendige idet efterfølgende laboratorie målinger ofte viser op til en hel pH-enheds forskel. I de senere år er man desuden blevet klar over at liquid junction potentialer kan give op til 0.2 pH fejl ved anvendelse af standard reference electroder med en keramisk stift. Disse fejl kan ikke opdages ved en almindeligt to buffer kalibrering.

Der blev udviklet en ny pH flow-celle, med en kapillær glas electrode og et reference electrode system med en "free-diffusion liquid junction". Udstyret blev afprøvet på laboratoriet og virkede

tilfredsstillende. Ved anvendelse af flow cellen under feltforhold opstod der imidlertid en række problemer med statisk elektricitet og dannelse af små gasbobler i kapillærerne. Disse problemer er endnu ikke blevet løst tilfredsstillende.

Rapportens tredje del omfatter en diskussion og vejledning i analyse procedurer for redox-følsomme komponenter i grundvandet. Den omfatter analyser af Fe^{2+}, H_2S, alkalinitet med Gran titrering, pH og O_2 med en sammenligning af electrode og Winkler metoden.

Rapportens sidste del indeholder en sammenligning af feltanalyser fra to forskeligge felt-teams. Feltanalyser er meget svært verificierbare, og procedurerne som anvendes under Losseplads og NPO Rabis Bæk projekterne blev derfor sammenlignet ved en fælles prøvetagnings tur til Vejen Losseplads. Resultaterne viste generelt en god overenstemmelse for Fe^{2+} og alkalinitet. pH målingerne viste en variation på ± 0.5 enhed og er forsat problematisk at måle mere nøjagtigt. O_2 bestemmelser, v.h.a. elektrode var ved koncentrationer under 1 ppm var upålidelige. Sammenligningen understregede behovet for en løbende kvalitets kontrol af feltanalyser.

ENGLISH SUMMARY

Postma, D., Hansen, E.Z. and Lyngkilde, J., 1990: Evaluation and development of methods for sampling and field analysis of groundwaters containing redox sensitive components. Losseplads-projektet, Report H-8.

It is the purpose of this report to evaluate and develop methods for high resolution groundwater sampling and of field methods for analysis of redox sensitive components.

First, a new multi-level single-hole groundwater sampler is described, which enables sampling of groundwaters without air contact. Additional all-plastic filtration equipment was developed, which allows in line anoxic filtration of the ground water sample and minimizes degassing. Performance tests of the equipment were carried out in 35 m deep wells in a sandy aquifer and show steep redoxclines and reproducible oxygen profiles. This indicates a good depth specific resolution of the device. A comparison of groundwater composition with sediment data from the same borehole, showed good consistency between the distribution of pyrite in the sediments and the disappearance of oxygen and nitrate with a sharp reaction front.

Next, the problems involved in measuring pH in poorly buffered groundwaters are evaluated. Comparison between field measurements and laboratory measurements show variations of up to one pH unit. Important aspects which may bias pH measurements are degassing, oxidation and temperature effects. More fundamentally are the problems concerning liquid junction potentials, which may yield

errors of up to 0.2 pH unit.

A new pH flow cell with a capillary glass electrode and a free-diffusion, renewable liquid junction, reference electrode was developed in order to avoid these problems. Although the flow cell performed well under laboratory conditions, substancial problems with static electricity and degassing were faced during use of the flow cell in the field.

Also a description and evaluation of methods for field analysis of redox sensitive components is presented. The main emphasis is placed on the colorimetric analysis of Fe^{2+}, H_2S, the GRAN titration of alkalinity, and pH-measurement and O_2 analysis by electrode including a comparison with the Winkler method.

Finally, an interlaboratory comparison of field techniques for redox sensitive components in groundwaters was made. In the two major groundwater programs presently carried out in Denmark, the Landfill project and the NPO project, field analyses form a integral part of the data collection scheme. The different field procedures used in the two projects were compared on a joint field trip to the Vejen Landfill. Field analysis were carried out for Fe2+, O_2, pH and alkalinity. Results showed generally good agreement for both Fe^{2+} and alkalinity. pH measurements varied by 0.5 unit and remain problematic. Finally, O_2 measurements made by electrode showed at low concentrations (less than 1 ppm) to be consistently unreliable.

INDHOLDSFORTEGNELSE

APPENDICES

1. INDLEDNING

Grundvandresourcerne bliver i stadig højere grad truet af forurening fra både punkt kilder, såsom lossepladser, og fra flade kilder som for eksempel anvendelse af kunstgødning på landbrugsjord eller sur nedbør. For at undersøge forureningens omfang og for at studere de processer som foregår i grundvands-magasinerne er der oftest brug for ganske detaljerede oplysinger om grundvandskemien som sjældent kan fås fra almindelige filtersatte boringer. Et særligt problem er desuden at vand fra iltfrie magasiner hurtigt ændrer sammensætning når vandprøven bliver bragt til jordoverfladen. Derfor er det nødvendigt at anvende særlige feltanalyseteknikker for at opnå pålidelige data på følsomme komponenter. Vores viden på dette område er under stærkt udvikling men dog langt fra fuldstændigt.

På denne baggrund har dette projekt til formål dels at udvikle og at evaluere metoder til detaljeret prøvetagning af grundvand, og dels at evaluere og forbedre feltanalysemetoder for grundvandsprøver med særlig vægt på redox-følsomme parametre.

2. GRUNDVANDSPRØVETAGNING

2.1 BESKRIVELSE AF EN NY MULTISAMPLER

Detaljeret dybde-specifik prøvetagning af grundvand kræver boringer som er specielt indrettet til dette formål som for eksempel multisamplere. I dette kapital beskrives og afprøves en nyudviklet multisampler til dybde-specifik prøvetagning af grundvand uden at prøverne kommer i kontakt med atmosfæren. Yderligere oplysninger kan findes i Appendix A1.

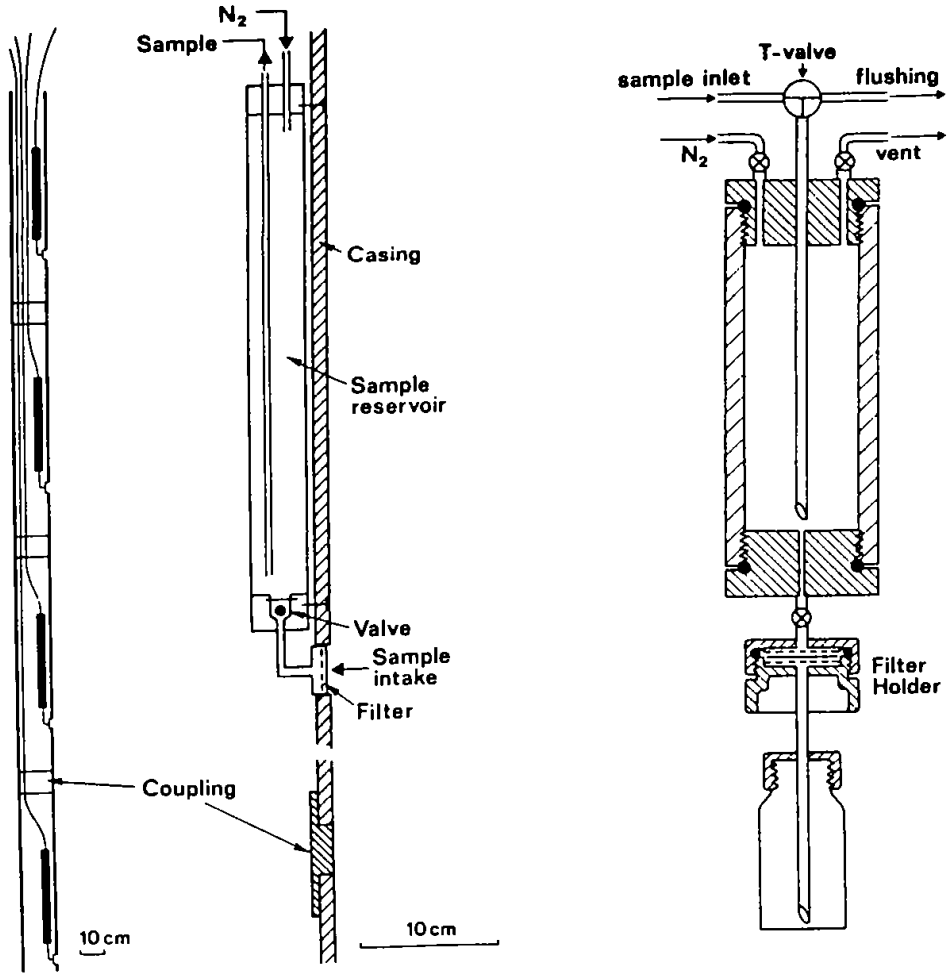

Fig. 1. Til venstre, multisampleren til udtagelse af niveau bestemte grundvandsprøver. Til højre, trykfiltreringssystemet som kan monteres direkte på prøvetageren til anoxisk filtrering af grundvandsprøver.

Multisampleren (Fig. 1) består af et ydre rør med indbyggede prøvetagere for hver meter. Systemet er opbygget af moduler af hver 1 m længde som består af et ydre rør med samle muffer og med en indbygget prøvetager. Vandet kommer ind i prøvetageren igennem et lille filter i det store rørs yderside. Prøvetagerne har en kontraventil i bunden samt et prøvereservoir på ca 250 ml hvorfra der fører to 4 mm slanger op til overfladen. Hele systemet er bygget i PVC og polyethylen og monteres permanent i en boring. Prøvetagningen foregår ved at anvende N_2 tryk på den ene slange af hver prøvetager, hvorved kontraventilen lukkes og prøven transporteres op til overfladen igennem den anden slange. På denne måde kan prøven opsamles uden at den kommer i kontakt med atmosfæren. En yderligere fordel er at systemet også kan anvendes hvor den umættede zone er mere end 10 m tyk, idet sugnings metoder her bliver uanvendeligt.

Desuden er der udviklet et trykfiltrerings udstyr (Fig. 1) som monteres direkte på prøvetagerne og som muliggør anoxisk filtrering af prøverne. Filterudstyret er konstrueret således at filterpatronen, selve filtret, samt prøveflasken kan skylles frit for ilt med N_2 inden prøven opsamles. Selve filtreringen foregår v.h.a. N_2-tryk igennem 0.1 μm membran filtre.

2.2 AFPRØVNING AF MULTISAMPLEREN

Udstyret er blevet afprøvet ved Rabis Bæk i sandede hedeslette-aflejringer hvor der udføres undersøgelser af nitrat reduktion i undergrunden. Der blev installeret 8 multisamplere ned til en dybde af 35 m.u.t. Resultaterne viser at skarpe redoxgrænser i magasinet kan registreres og reproduceres.

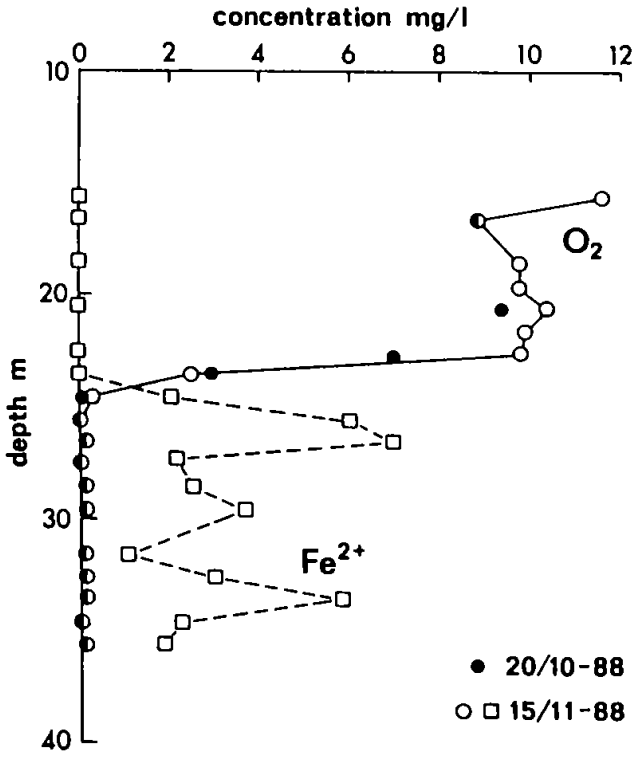

Fig. 2. Koncentrationer af Fe^{2+} og O_2 i et hedeslettemagasin ved Rabis Bæk. Iltmålingerne blev foretaget på to forskellige datoer.

Dette er demonstreret i Fig. 2 som viser en iltholdigt øvre grundvandslag skarp adskilt fra en nedre anoxisk, Fe^{2+}-holdigt zone. Iltmålingerne blev gentaget en måned senere og de to data er stort set identiske, hvilket beviser reproducerbarheden af prøvetagnings systemet.

Variationer i grundvandskemien vil i mange tilfælde afspejle reaktioner imellem opløste ioner i grundvandet og mineraler i sedimentet. Ved Rabis Bæk blev der samtidigt med installationen af multisamplere taget sediment kerner. Sammenhængen imellem grundvandskemien og sedimentets pyrit (FeS_2) indhold er illustreret i Fig. 3

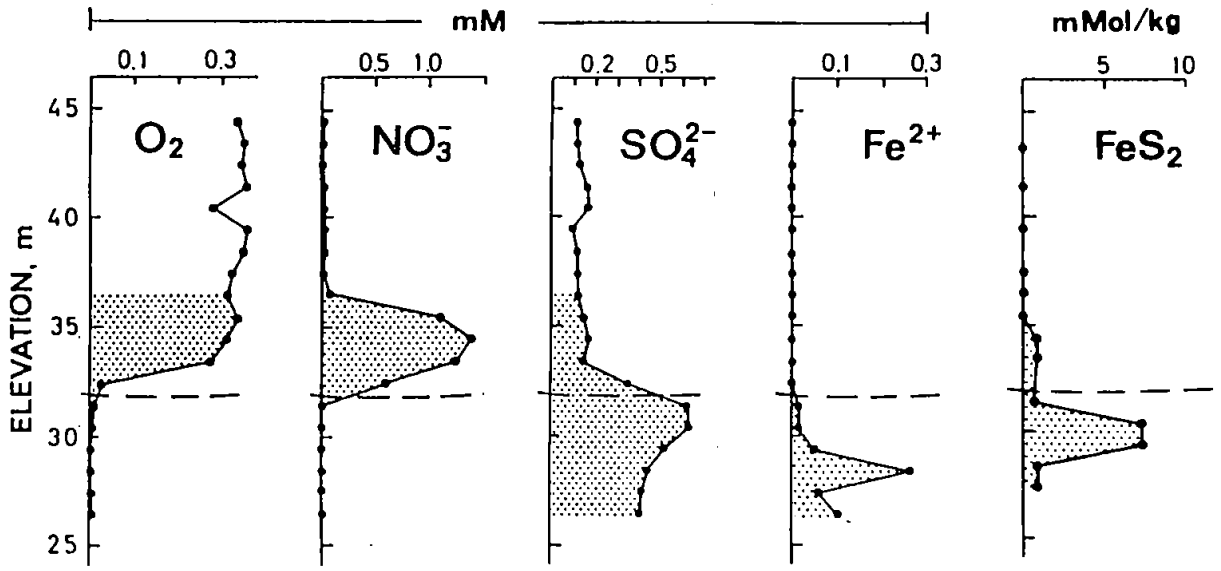

Fig. 3. Sammenhængen imellem grundavndskemien og sedimentets pyrit (FeS_2) indhold ved Rabis Bæk. De rastede del af kurvene indikerer vand som stammer fra landbrugs områder.

Processen som foregår ved redoksklinen er antageligt oxidation af pyrit ved grundvandets nitrat- og iltindhold og som resulterer i stigende sulfat og jern koncentrationer. Bemærk den meget fine overenstemmelse med sedimentets pyritindhold.

3. pH-MÅLING I GRUNDVAND MED LAV BUFFERKAPACITET

3.1 FELT- OG LABORATORIUMMÅLING AF pH

En stor del af de kalkfrie jyske hedeslettemagasiner har grundvand med en meget lavt bufferkapacitet og er i særligt grad følsomme for forsuringsprocesser. Det er derfor af stor betydning at kunne indsamle pålidelige pH data fra disse magasiner hvilket dog vanskeliggøres af den lave bufferkapacitet. Fig. 4 viser en sammenligning af pH værdier fra et sådan magasin dels målt i laboratoriet efter hjemtransport og dels målt i felten direkte efter prøveudtagning.

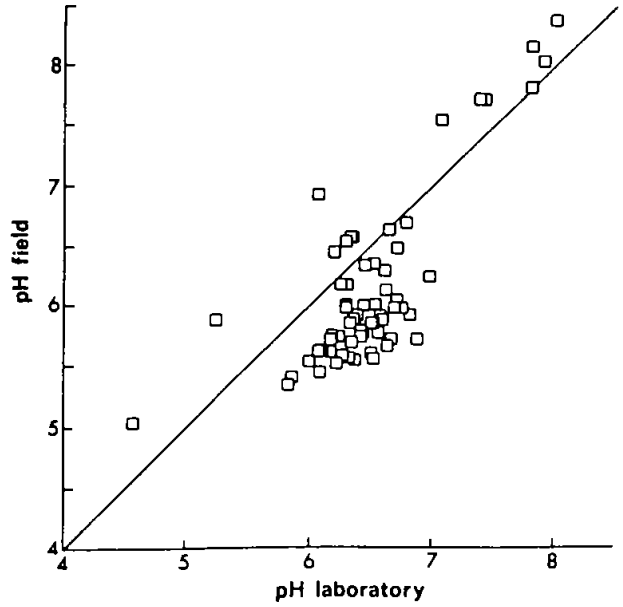

Fig. 4. Sammenligning af pH målinger udført i felten direkte efter prøveudtagning, med pH målinger udført på laboratoriet efter hjemtransport af prøverne. Målingerne er udført på grundvandsprøver fra Rabis Bæk.

Der observeres i Fig. 4 betydelige forskelle imellem felt og laboratoriet målinger som kan beløbe sig op til en hel pH-enheds

forskel. Årsagen til disse forskelle er en række fejlkilder ved pH målinger når de udføres i laboratoriet på et senere tidspunkt. Disse omfatter temperatursændringer, afgasning af CO_2, oxidation m.v. I de senere år er man desuden blevet klar over at liquid junction potentialer kan give op til 0.2 pH fejl ved anvendelse af standard reference electroder med en keramisk stift (se Appendix A2 for yderligere detaljer). Disse fejl skyldes variationer i liquid junction potentialet afhængigt af opløsningens sammensætning, og sådanne fejl opdages ikke ved en almindeligt to buffer kalibrering, idet der her altid bruges buffer opløsninger med en høj ionstyrke.

3.2 BESKRIVELSE OG AFPRØVNING AF EN NY pH FLOW CELLE

I en forsøg på at forbedre pH-målinger i grundvandsprøver med en lav bufferkapacitet blev der udviklet en ny pH flowcelle hvor problemerne med liquid junction potentialer kan undgås.

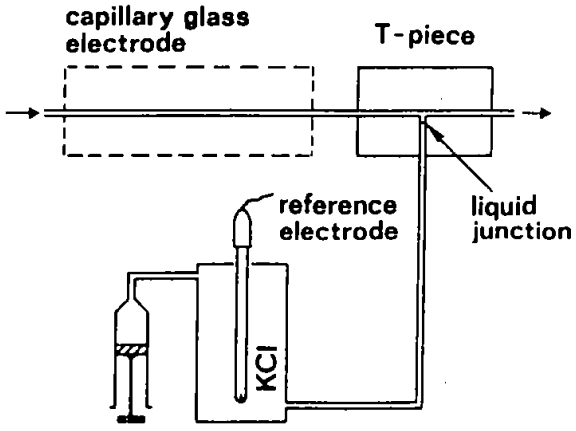

Fig. 5. Principskitse af en nyudviklet flowcelle til pH måling.

Flow cellen (Fig. 5), består af en kapillær glas electrode og et reference electrode system med en "free-diffusion liquid junction" som kan fornyes. Forbindelse til referenceelectroden foregår her via en saltbro hvor kontaktet med prøven opnås i T-

stykkets sidearm. Her findes en veldefineret grænseflade imellem prøveopløsningen med lav ionstyrke og den koncentrerede KCl opløsning fra reference systemet. Ved hjælp af stemplet trykkes en smule KCl opløsning ud igennem T-stykket og grænsefladen fornyes således at målingens reproducerbarhed kan testes. Udstyret blev afprøvet på laboratoriet og virkede tilfredsstillende. Ved anvendelse af flow cellen under feltforhold opstod der imidlertid en række problemer med statisk elektricitet og dannelse af små gasbobler i kapillærerrørene.

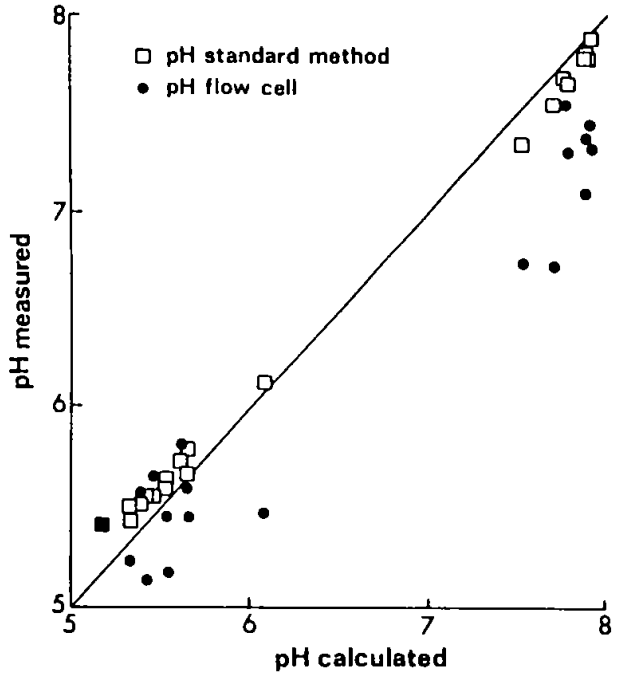

Fig. 6. Sammenligning af pH værdier målt i felten med pH værdier beregnet ud fra alkalinitet og TIC v.h.a. en computer model. Standard metoden omfatter måling med en kombineret glaselektrode direkte efter prøveudtagning mens flow cell målinger er udført med den nyudviklede flowcelle monteret direkte på grundvands prøvetageren. Målingerne er udført ved Rabis Bæk.

Disse problemer er endnu ikke blevet løst tilfredsstillende. pH-målingerne blev kontrolleret ved at sammenligne dem med pH-

værdier beregnet ud fra alkalinitet og total opløst uorganisk kulstof (TIC) v.h.a. en specierings model. I en sådan model omregnes koncentrationer til aktiviteter og vandige komplekser beregnes, herunder dem fra karbonatsystemet.

Figur 6 viser at der er dårlig overenstemmelse imellem beregnede værdier og flowcellemålinger, som skyldes hovedsageligt de ovennævnte problemer med boble dannelse og statisk elektricitet. Derimod er vores standard felt pH-målinger, som er udført med en kombineret glaselektrode direkte efter prøveudtagning, i meget fint overenstemmelse med de beregnede værdier idet afvigelserne er indenfor 0.1 pH enhed. Dette viser således at det er muligt at opnå en konsistent dataset, bestående af pH, alkalinitet og TIC for det opløste karbonat system.

4. FELTANALYSER: PROCEDURER OG PROBLEMER

I Appendix A3 presenteres en omfattende diskussion og vejledning i analyseprocedurer for redox-følsomme komponenter i grundvandet. Problemer omkring Fe^{2+} analyse diskuteres især med henblik på dens meget hurtige oxidation omkring neutralt pH. Der anbefales kolorimetrisk feltanalyse v.h.a. ferrozin metoden. H_2S analyser kan dels påvirkes af afgasning af H_2S og dels af oxidation. Det anbefales at prøverne samles direkte op i en zink-acetat opløsning, med efterfølgende kolorimetrisk analyse.

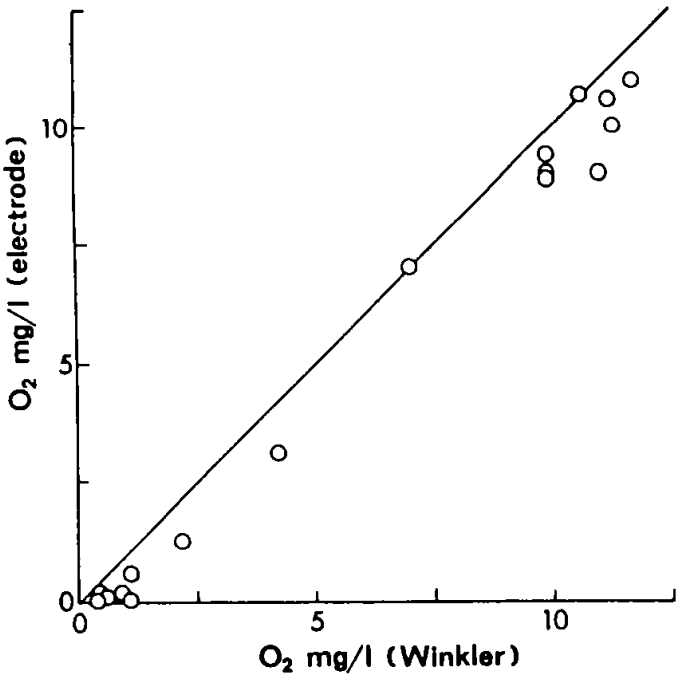

Fig. 7. Sammenligning af iltmålinger på grundvand v.h.a. elektrode og v.h.a. den traditionelle Winkler metode.

Til feltmålinger af alkalinitet anbefales Gran titrering stærkt, idet man her ikke er afhængigt af at ramme omslagspunktet precist. Der er udviklet en Lotus makro til beregning af Gran-plots.

Procedurer for feltmålinger af pH beskrives sammen med en procedure for at teste elektrodernes respons. Endeligt beskrives proceduren for feltmåling af O_2 med en elektrode monteret i en flowcelle koplet direkte op på prøvetagningssystemet. Elektrode måling af O_2 er testet overfor den traditionelle Winkler metode (Fig. 7). Der er generelt en god overenstemmelse imellem de to metoder. De afvigelser som findes kan lige så vel skyldes selve prøvetagnings proceduren som er forskellig for de to metoder, som måleteknikken. Dog vides at elektrode målinger ved koncentrationer under 1 mg/l bliver upålidelige.

5. SAMMENLIGNING AF FELTPROCEDURER

Dette kapitel indeholder en sammenligning af resultater af feltanalyser fra to forskeligge felt hold. Se Appendix A4 for yderligere detaljer.

Feltanalyser er meget svært verificierbare, og det var derfor nyttigt at sammenligne de procedurer som anvendes af Laboratoriet for Teknisk Hygiejne (LtH) indenfor Lossepladsprojektet og dem som Instituttet for Teknisk Geologi (ITG) har brugt ved Rabis Bæk under NPO projektet. Dette blev gjort ved en fælles prøvetagnings tur til Vejen Losseplads. Her blev der foretaget feltanalyser på langs af forureningsfanen fra dybdespecifikke filtre. Analyserne blev foretaget samtidigt af de to hold på de samme grundvandsfiltre. Resultaterne er vist i Fig. 8 hvor de fuldoptrukne linier angiver én til én korrelationen. Til alkalinitetsbestemmelse brugte begge hold Gran titrering, men med forskellig prøvemænde og titreret med forskellig syrestyrke. I de fleste tilfælde er der en meget fin overenstemmelse imellem resultaterne af de to hold. I enkelte tilfælde er der ganske store uoverenstemmelser, som næppe kan skyldes almindeligt måleusikkerhed, men snarere må skyldes decideret fejlmanipulation af prøvemængder m.v.

pH blev målt af LtH med en flowcelle med en kombineret glaselektrode og af ITG med en kombineret glaselektrode på en delmængde af prøven direkte efter udtagning. Resultaterne er jævnt fordelt omkring én til én korrelationen, men med indbyrdes afvigelser på op til 0.5 pH enhed. Det bekræfter igen at nøjagtige pH målinger er svært at opnå.

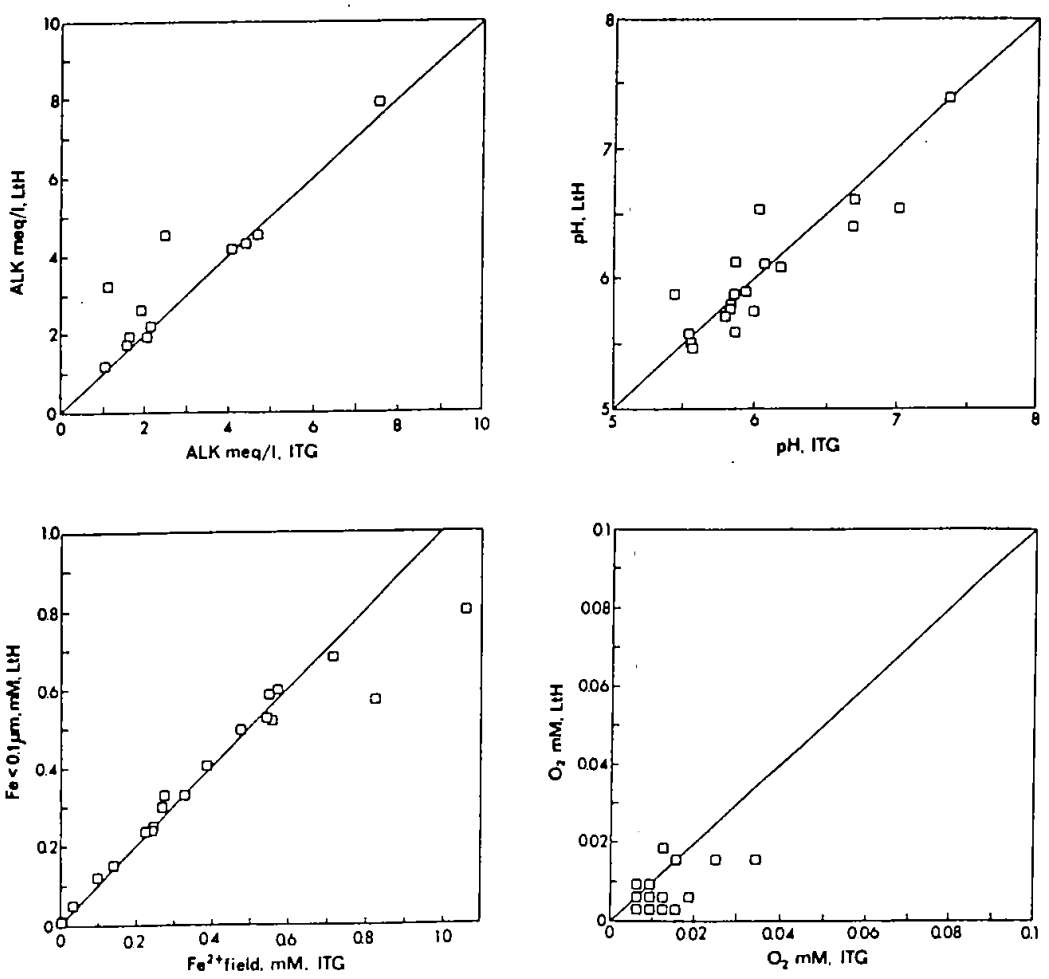

Fig. 8. Sammenligning af feltanalyseresultater ved samtidig prøvetagning af hold fra LtH og ITG. Linierne angiver en til en korrelationen. Prøvetagningen blev foretaget ved Vejen Losseplads.

For Fe^{2+} blev der brugt ret forskellige teknikker; ITG anvendte kolorimetrisk analyse af Fe^{2+} direkte i felten, mens LtH filtrerede prøverne igennem 0.1 μm og målte total Fe indhold v.h.a. AAS. Under fuld reducerede forhold burde der kun være Fe^{2+} i opløsning og overenstemmelse med ITG's felt kolorimetriske bestemmelser er generelt også ganske god.

Endeligt blev O_2 analyserne af begge hold målt v.h.a. en

elektrode monteret i en flow celle, under anvendelse af identisk måleudstyr. Da der var tale om reduceret vand er iltindholdet i prøverne ganske lavt. Der fandtes imidlertid ganske store afvigelser i måleresultaterne fra de to hold, som bekræfter at ilt målinger v.h.a. elektrode ved koncentrationer under 1 mg/l er upålideligt. Generelt understregede sammenligningen behovet for en løbende kvalitets kontrol af feltanalyser.

APPENDIX A1

A NEW GROUNDWATER MULTISAMPLER AND SAMPLE RETRIEVAL SYSTEM WITHOUT AIR CONTACT

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ABSTRACT

For a study of nitrate reduction processes in a sandy aquifer, a new multi-level, single-hole groundwater sampler was developed, which enables sampling of groundwaters without air contact. Water was sampled at each level by means of a gas driven double line sampling device with a contra valve located near the entrance of the water into the sampler. Additional all-plastic filtration equipment was developed, which allows in line anoxic filtration of the ground water sample and minimizes degassing.

Performance tests of the equipment in 35 m deep wells showed steep redoxclines and reproducible oxygen profiles. This indicates good depth specific resolution of the device. However, some degassing within the downhole installation seems to occur at the gas water interface. Therefore, care should be taken to discard the first part of the sample for measurement of gasses and pH.

Comparison of groundwater composition with sediment data from the same borehole, at the site of pyrite oxidation by oxygen and nitrate shows good consistency between the distribution of pyrite in the sediments and the disappearance of oxygen and nitrate with a sharp reaction front.

INTRODUCTION

Ubiquitous problems in groundwater pollution emphasize the need of high resolution sampling. In addition, the increasing application of coupled geochemical-transport models to processes occurring in aquifers require high quality data to validate such models. Different approaches have been used to obtain depth specific ground water samples (Cherry, 1983). Basically these can be divided in multiple-borehole piezometer nests, multiple-level, single borehole piezometers and single borehole packer sampling (Andersen, 1979; Oberman, 1982). Single hole multiple piezometers can be installed as bundles (Cherry et al, 1983; Appelo et al., 1982) or enclosed in a casing (Pickens et al., 1978; Stuyfzand, 1983; Leuchs, 1988). While the first approach is by far the cheapest, it requires cohesionless aquifer material while a inherent risk of short circuiting between different sample levels through the bundles of tubing remains to exist. This risk increases with the number of sample levels used and differences in hydraulic head.

Sample retrieval is done most easily by suction up to depths of about 9 m. However, the application of vacuum will result in serious degassing of the sample (Suarez, 1987; Stuyfzand, 1983) and thus produce erratic results for both dissolved gasses and pH. Alternative approaches are pressure operated downhole syringe pumps (Gillham and Johnson, 1981), or double line gas driven sampling devices (Appelo et al., 1982).

For a study of nitrate reduction in a sandy aquifer, we needed a detailed knowledge of both sediment chemistry and concurrent groundwater chemistry. Further requirements were repeated and

reproducable water sampling, and since we were dealing with a redox problem, sample handling without air admission. For this purpose, we developed a encased single hole multisampler, operated with a double line gas driven sampling device. Additional sample retrieval equipment enables filtration and measurements of redox sensitive components without air contact.

MULTISAMPLER

The multisampler is constructed in units of one meter 140 mm ø PVC piping. Each unit contains an all PVC water sampler fitted in the inside of the pipe (FIG. 1). The water sampler has an approximate volume of about 250 ml and is equipped with a contra-valve at the base. The valve consists of a teflon ball seated on a teflon bed. It is important that the valves are manufactured accurately so they are gas tight. Otherwise, the gas used to empty the sampler may enter the aquifer. The water enters the sampler through a 40 μm nylon screen, to avoid introduction of fine material which could block the valve mechanism. From the top of the sampler, two 4 mm polyethylene tubes lead to the surface. The first is used to pressurize the sampler with N_2 and is fitted at the top of the sampler (FIG. 1). The second transports the sample up to the surface and is placed at the bottom of the water sampler. Every other sampler is modified to allow measurement of the hydraulic head. In that case, only one 11 mm nylon tube is fitted at the top of the sampler, large enough the allow lowering of a small pressure transducer for measuring the hydraulic head. When water sample has to be retrieved from these samplers, a 4 mm polyethylene tubing is lowered inside the nylon tubing down to

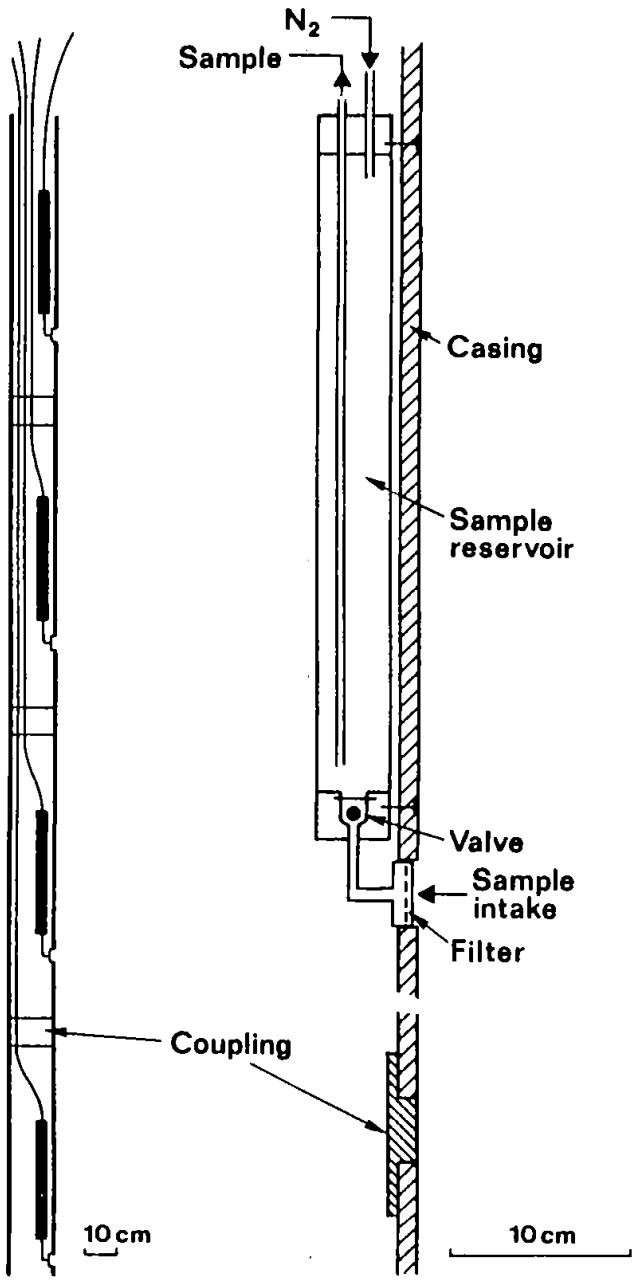

FIG. 1 A Schematic drawing of the multisampler system, with at the left the PVC outer casing constructed of one meter units with a water sampler each and at the right hand an enlarged display of the water sampler. Each second sampler was fitted with a larger nylon tube at the top to allow measurement of the hydraulic head.

the bottom of the sampler.

When the multisampler is installed, in our case with a total lenght of 30-35 m, sections of 1 m each containing a sampler are lowered into the borehole subsequently. Each unit is fitted at the head of the casing to the previous ones by means of coupling units (FIG 1.). In this way, the sampler remains centered inside the casing, Lenghtes of up to 6 m of blind piping corresponding to the unsaturated zone, are finally fitted.

The multisampler has an outer diameter of 140 mm and is to be placed in a 4" (152 mm) casing. This yields a space of 6 mm between the sampler and the casing and requires that the multisampler is completely smooth on its outer surface. Care should be taken during installation of the multisampler that no object may wedge itself in the narrow space. The close fit between the multisampler and the innner casing diameter was adopted to ensure that the aquifer material collapses tight onto the surface of the multisampler upon withdrawal of the casing. This is necessary in order to avoid short-circuiting between different sample levels.

FILTRATION UNIT

The filtration unit consist of a reservoir of heavy polycarbonate pipe fitted with teflon caps and sealed with O-rings with a commercial 50 mm polycarbonate filter holder (FIG.2). Membrane filters with a pore size of 0.1 μm were used as the best compromise between a reasonable flow rate and removal of most particulate material (Kennedy and Zellweger, 1973; Laxen and Chandler, 1982). The reservoir including the filter and sample bottle are flushed with N_2 in order to exclude all atmospheric oxygen. This is

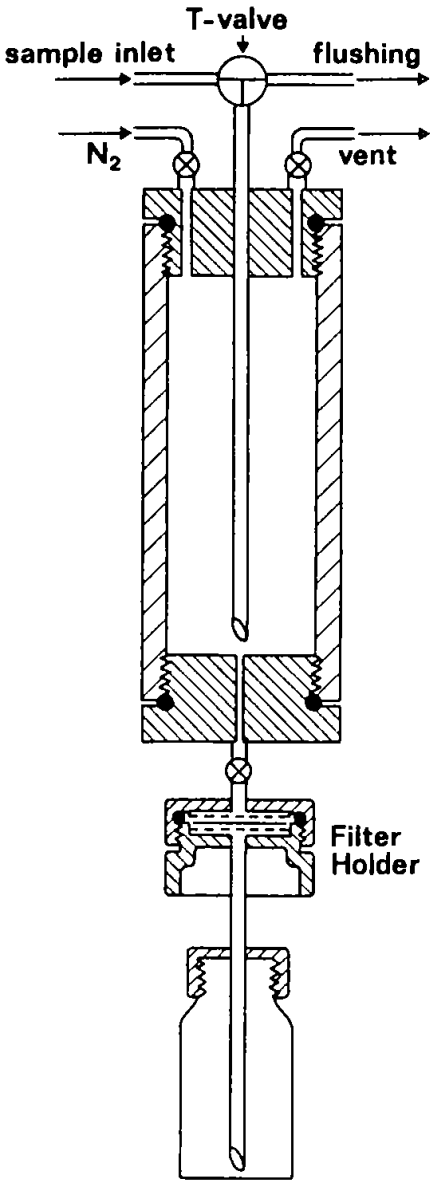

FIG. 2 The all teflon and polycarbonate filtration unit which is fitted directly to the sampler outlet and allows anoxic transfer and filtration of the water sampler.

important, because O_2 adsorbed on the filter material may give erratic results for both Fe^{2+} (Troup et al., 1974) and phosphate (Bray et at., 1973).

The sample enters the reservoir through a T-valve. The inlet is connected directly to the outlet of the sampler, thereby eliminating any air contact from the water sample. The T-valve allows draining the first part of the sample until bubble free water comes up. The T-valve is then turned clockwise so that the sample enters the reservoir. The outlet into the reservoir, and into the sample bottle, are placed in the bottom in order to avoid the significant degassing which would take place when the sample drips into the reservoir. It requires that the T-valve is turned back before the sampler is emtied completely since upcoming N_2 otherwise would bubble through the sample. However, this is easily avoided as the last part of the sample from the minifilter start to flow at a much higher rate. This arrangement enables sample retrieval and filtration whithout any air contact and with a minimum of degassing.

OPERATION

Eight multisamplers of 30 to 35 m total lenght and each containing about 20 water samplers, were installed in a cohesionless sand aquifer, near Rabis Creek, Denmark. The sediments are fluvioglacial sand deposits of medium grain size without important changes in lithology. The groundwater level at the site is about 15 m below the surface.

After the installation of the multisamplers was completed, they were left alone for a period of three months in order to allow

fine material, suspended by the drilling operations, to settle in the aquifer. At groundwater flow rates in the area of study, ranging from 40 to 60 m per year, this period of rest should ensure the renewal of groundwater which could have been affected by drilling operations by many pore volumes. Then each sampler was emptied at least 5 times, until clear water samples were obtained. As a further check on the complete removal of any contaminated groundwater, the water in the borehole was previous to the installation of the multisampler spiked with LiCl. An equal distribution of the LiCl over the entire depth range of the boring was ensured by lowering a lenghts of tubing, filled with concentrated LiCl and closed at the surface end. When the lower end reached the bottom of the casing, the upper end was released and the tubing gently raised while released LiCl over the entire lenght of the water column. Note also that LiCl trapped inside the casing of the multisampler, will remain there and indicate any leakage in the sampling system. The initial concentration of LiCl in the borehole water was 1 mMole/l. After 3 monthes Li was below detection limit (0.01 mMole/l) except in a few samplers placed in fine grained intervals and a single defective sampler. Hydraulic head measurements were carried out on every other water sampler which was equipped for this purpose, but showed no significant differences (less then 2 cm) between different samplers in each boring.

The performance of the multisamplers was tested using field measurements of a number of redox sensitive components. Oxygen and pH were measured with flow cells directly coupled to the outlet of the samplers, arranged such as to allow discarding the first

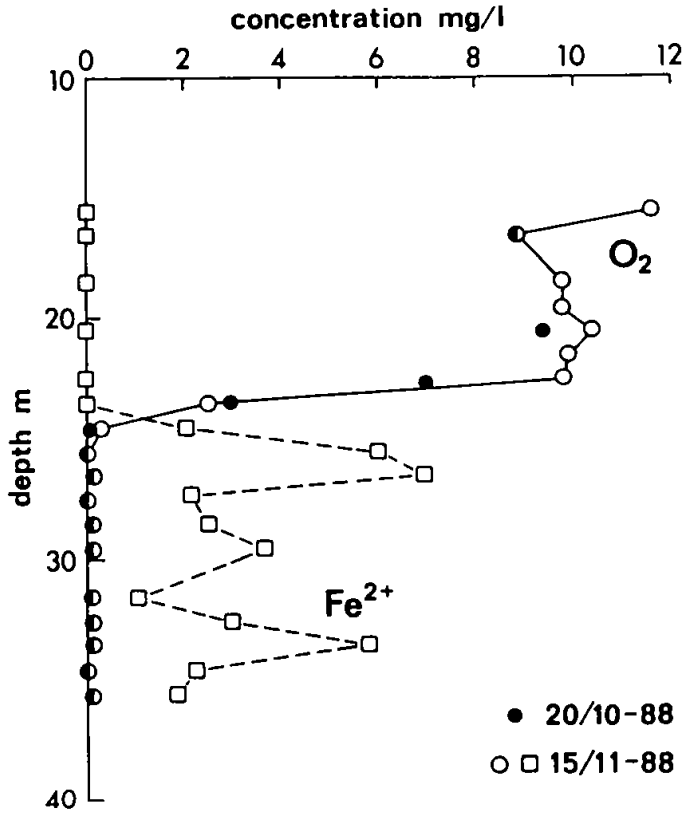

FIG. 3 Oxygen and Fe^{2+} profiles obtained with the multisampler. Oxygen profiles were repeated at two different dates. Note the sharp interface between oxic and anoxic zones.

part of the sample which could contain bubbles. The values measured as a function of the amount of sample retrieved were monitored with a recorder. Fe^{2+} was measured colorimetrically (Stookey, 1970) immediately after anoxic filtration using a Dr Lange battery driven semi-double beam spectrophotometer. Some results are presented in FIG 3. It show an upper oxic part of the aquifer, with more or less constant oxygen concentrations, separated by a very sharp interface from the anoxic zone. The oxygen profile was repeated about one month later and could be

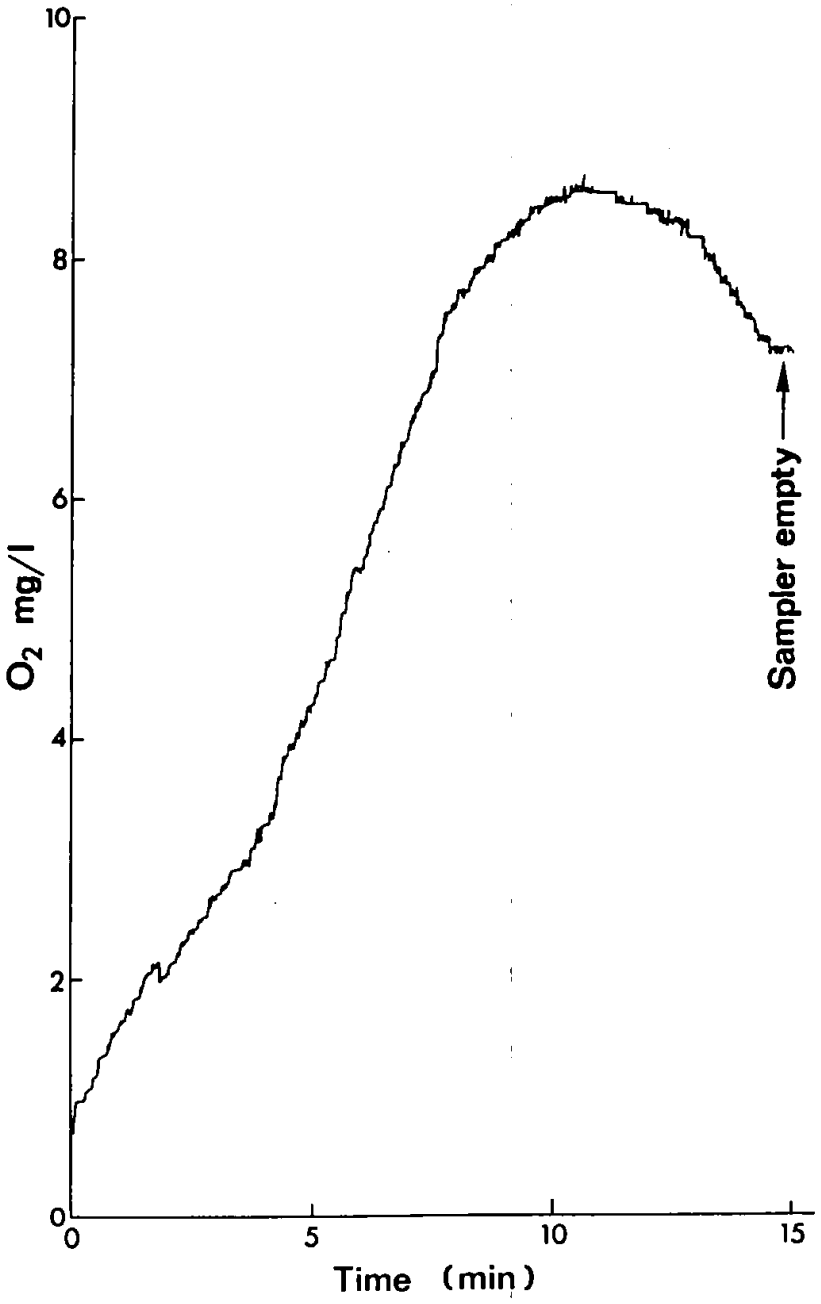

FIG. 4 The change in oxygen concentration as a function of the retrieved sample volume, corresponding to time. The sample was taken from a 22 m deep level, reflecting oxygen rich waters in a sandy aquifer.

reproduced closely. This is taken as evidence for good spatial resolution of the multisampler.

Some words of caution with respect to sample degassing are, however, appropriate. At deeper oxygen-containing samplers, it was noted that the oxygen concentration changed with the volume of sample recovered. This is illustrated in FIG. 4, for a high oxygen sample retrieved at 22 m depth. One observes that the oxygen concentration initially increases with the volume of sample retrieved (as reflected by time), then after passing a maximum, the oxygen content decreases again somewhat. The explanation for this behavior is apparently that emptying the sampler before sampling, leaves the whole sample system, including tubing to the surface filled with N_2. When the oxygen rich water sample enters the sampler and is recovered by applying N_2 pressure, some degassing apparently occurs at the water/gas interface in the two rising tubes. The terminal decrease in oxygen concentration reflects the water originally standing in the pressure tube. It is clear that the initial sample volume always should be discarded for measurement of gasses or pH and furthermore that preferably a concentration plateau should be attained.

An important aspect for our purposes is the consistency between groundwater chemistry and the sediment chemistry in the same boring. It appears that nitrate in our aquifer becomes reduced by minor amounts of pyrite in the sediments. The process is illustrated in FIG 5. Note again the sharply delineated redoxcline as reflected by the abrupt and simultaneous disappearances of nitrate and oxygen. The oxidation of pyrite is reflected by the increase in dissolved sulfate concentrations. These changes in

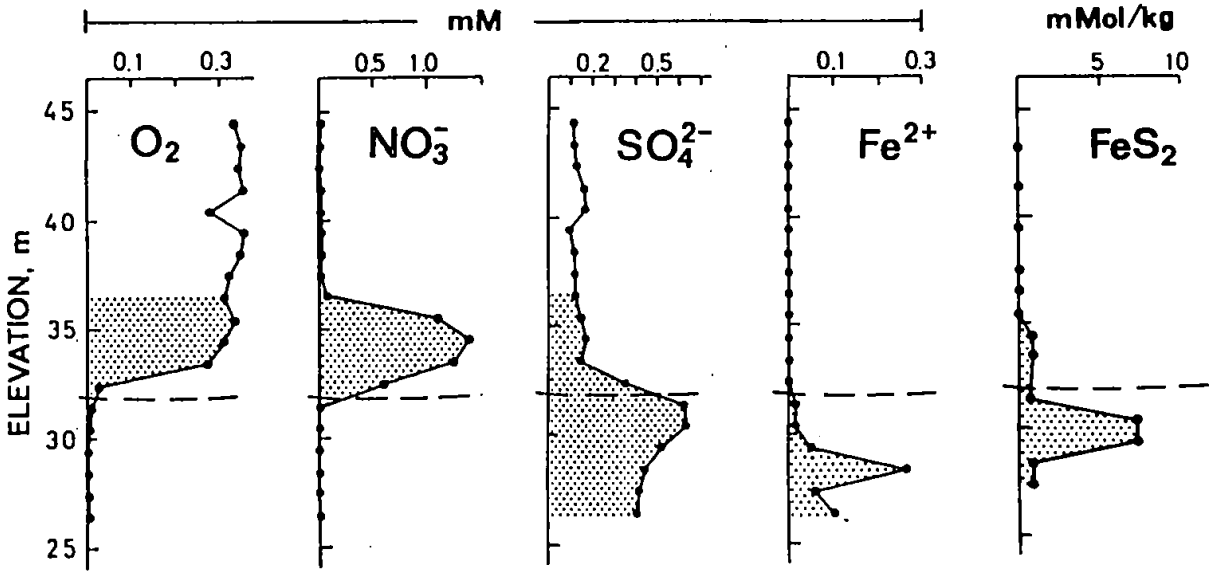

FIG. 5 Concentration profiles in groundwater and sediments at the site of pyrite oxidation by oxygen and nitrate in a sandy aquifer. Note the sharp reaction front and the good agreement between groundwater and sediment compositions.

water chemistry are perfectly matched by the distribution of pyrite in the sediment. Above the redoxcline in the oxygen and nitrate containing layers, all pyrite has been removed, and across the redoxcline a sharp increase in pyrite contents is observed. Both the sharp concentration profiles and the agreement with sediment data gives us confidence in the good performance of the multisampler system.

ACKNOWLEDGEMENTS

The development and construction of the multisampler reflects a joint effort of the Geological Survey of Denmark and the Institute of Applied Geology. Special thanks are due to Niels Paul Pedersen who took care of the technical construction aspects and Ellen Zimmer Hansen and Søren Nielsen were indispensible members of the field crew.

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APPENDIX A2

PH MEASUREMENTS OF GROUNDWATERS: EVALUATION AND DEVELOPMENT OF A NEW FLOW CELL FOR FIELD USE

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ABSTRACT

The significance, and problems involved in measuring pH in poorly buffered groundwaters were evaluated. Comparison between field measurements and laboratory measurements show variations of up to one pH unit. Important aspects which may bias pH measurements are degassing, oxidation and temperature effects. More fundamentally are problems with the liquid junction potential which may yield errors of up to 0.2 pH unit. Such errors are due to variations in the liquid junction potential depending on the composition of the solution. Since all commercial buffer solutions have a high ionic strenght, malfunctioning electrode pairs will not be revealed by standard buffer calibration procedures.

A new pH flow cell with a capillary glass electrode and a free-diffusion, renewable liquid junction, reference electrode was developed in order to avoid these problems. Although the flow cell performed well under laboratory conditions, substancial problems with static electricity and degassing were faced during use of the flow cell in the field. Comparison of flow cell pH measurements with those obtained by careful standard methods showed a great deal of scatter but no systematic differences. Measured pH values were compared with those calculated from TIC and alkalinity using a speciation model. Calculated pH values did not agree well with flow cell pH. Therefore, we consider pH flow cell measurements as unreliable until the problems with static electricity and degassing are solved. On the other hand, calculated pH values were in very good agreement with pH measured by our standard method, which indicates that a consistent set of parameters in the carbonate system can be obtained.

INTRODUCTION

The measurement of pH in natural waters is an procedure routinely carried out by large numbers of environmentalists. For order of magnitude estimates, it is a quite unproblematic parameter. However, to obtain meaningful pH measurements in terms of hydrogen ion activity is, particularly in poorly buffered waters, much more problematic. This has been actualized by the increasing application of chemical speciation models for saturation calculations in groundwater chemistry. Often, such models require an accuracy of pH-measurements which is better than 0.05 pH unit, and this is very difficult to obtain by standard procedures. Also increasing acid rain problems have emphasized the need for more reliable pH measurements (McQuaker et al., 1983).

The problems involved in pH measurements of groundwaters are manifold. Some are related to the removal of groundwater from its <u>in situ</u> position during sampling. These include degassing of CO_2, which will increase the pH and also may cause precipitation of $CaCO_3$ (Suarez, 1987). Others concern the oxidation of Fe^{2+} and precipitation as FeOOH, and are analoguous for other oxidizable species like H_2S, which may seriously affect pH values. Most of this type of problems can be overcome by careful sampling and field measurement procedures.

Other sources of error particularly concern the liquid junction between the calomel electrode and the solution to be measured. The fundamental problem is that the liquid junction potential across the porous ceramic plug of the calomel electrode

will vary with the composition of the solution to be measured (Bates, 1973). In seawater and brackish waters, this has led to the development of special pH scales (see Millero, 1986 and references therein). Liquid junction problems in low ionic strenght waters have been recognized quite recently (Illingworth, 1981; Brezinski, 1983; Davison and Woof, 1985) and may amount to several tens of a pH unit. A tricky aspect of this type of errors is that they are not revealed by a standard two buffer calibration (Illingworth, 1981; Davison and Woof, 1985), since commercial buffers all are high ionic strenght solutions. Electrode performance should therefore be checked in dilute solutions and malfunctioning is also indicated by large (>0.02 pH unit) potential shifts between stirred and unstirred solutions (Davison, 1987).

The uncertainties involved in routine pH measurements were illustrated in an interlaboratory comparison, with ten parcipitants, each measuring the pH of poorly buffered freshwaters in the field and laboratory. Total errors of pH measurement for samples brought to the laboratory were estimated to ± 0.2 pH, while larger errors were observed for field measurements.

Attempts to solve the liquid junction problems have used renewable free diffusion liquid junctions, formed in a cylinder as a sharp boundary between electrolyte and sample, instead of the ceramic plugs employed in most commercial reference electrodes. In some cases, the free diffusion liquid junction is formed in a capillary immersed in a reaction vessel (Brezinski, 1983 and the Hach One electrode), while in other cases a flow cell is used were the free diffusion liquid junction is formed in a T-piece. (Covington et al., 1983, 1985; Harbinson and Davison, 1987).

Generally, the free diffusion liquid junction reference electrodes appear to yield much more reliable pH measurements in low ionic strenght waters. However, at their present stage of development, they are far from suitable for routine field use.

It is the purpose of this paper, to evaluate common practices of field pH measurements, and furthermore to develop and test a free diffusion liquid junction flow cell suitable for field use.

METHODS

Standard pH measurements were carried out with a WTW pH196 instrument, equipped with automatic two buffer calibration and a Radiometer GK2401C combination electrode. Commercial Radiometer 4.01, 7.00 and 9.18 buffer solutions were used for calibration. Buffer solutions and electrode were brought to in situ groundwater temperatures before measurement. pH was measured in open 30 ml plastic vials, immediately after recovery of the sample, on a quiescent solution after initial gentle stirring. When a stable potential was reached, a new subsample was taken and the measurement repeated to ensure that a reproducible potential was obtained. Procedures for use of the new flow cell are described elsewhere in this report.

TIC samples were taken by filling sample glasses directly from the ground water sampler, replacing at least two volumes and capping with teflon septa without trapping gas bubbles. The samples were stored cool and analysed as soon as possible. Analysis was done on a Dohrman DC180, and involves acid addition, stripping of CO_2 and detection by IR.

Alkalinity was measured in the field, immediately after sample

recovery employing the GRAN titration method. Details are given elsewhere in this report.

RESULTS

Our evaluation of pH measurements on groundwaters started with a comparison of measurements carried out in the field using a open vessel replenishment method (henceforth called standard method), and routine measurements carried out back in the laboratory at the Geological Survey of Denmark. The groundwaters at the field site are poorly buffered, with a low ionic strength and contain in their reduced parts up to 15 ppm Fe^{2+}. They were sampled from depth specific double line gas driven devices, incorporated in a multi-sampler, as described elsewhere in this report.

The results are displayed in Fig. 1 and show considerable variation between field and laboratory measurements. Differences between the two sets of data may amount to up to one pH unit and seem to emphasize the necessity of field measurements. Apparently there are no systematic differences; a large group of data points between pH 6 and 7 show higher laboratory values, which could indicate degassing of CO_2, but the remaining data displays higher field values. Thus no simple correction of laboratory pH data appears possible. Even though the field measurements are believed to be more reliable than laboratory measurements, they still can be biased by liquid junction errors. It was therefore decided to develop and test a flow cell with a free diffusion liquid junction suitable for field use.

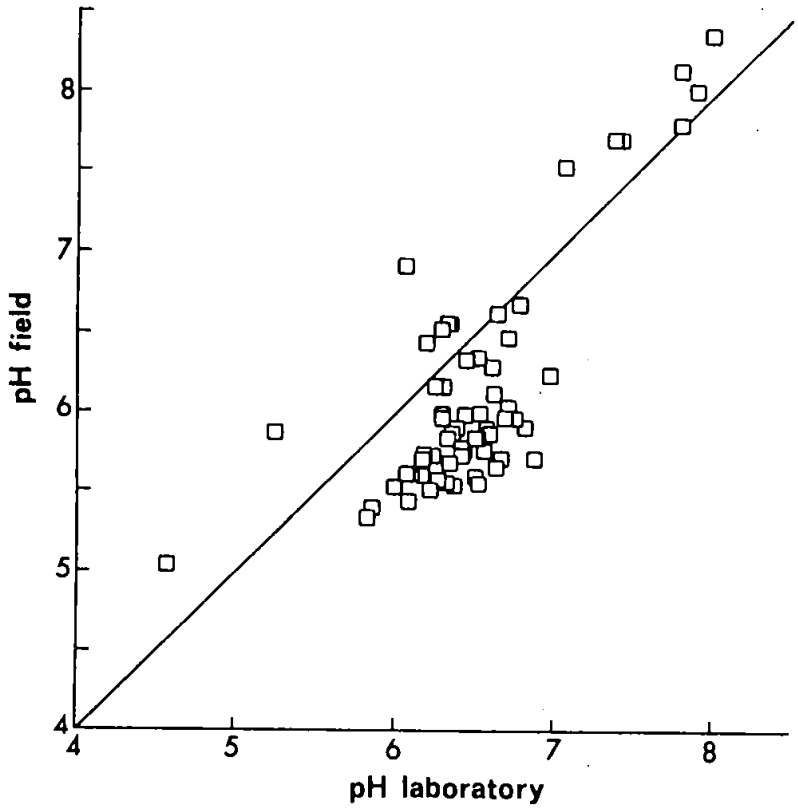

FIG. 1 A comparison of pH measurements carried out in the field, by the standard method, and laboratory measurements on poorly buffered groundwater near Rabis Bæk, Denmark.

Conctruction of the pH flow cell

The basic idea in the design of the flow cell, was to combine a commericially available capillary glass electrode (Radiometer G299A) with a T-piece type free diffusion junction. The perspex T-pieces developed by Harbinson and Davison (1987), which have proven to function well, are particularly suitable for field use due to their robustness. The construction of the flow cell is shown schematically in Fig. 2. The sample passes subsequently

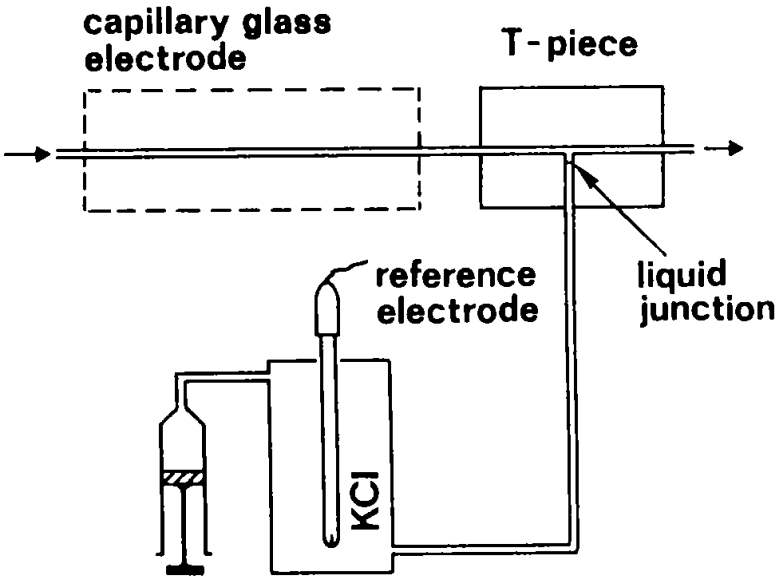

Fig. 2 A schematic drawing of the free diffusion liquid junction flow cell for pH measurement.

through the capillary glass electrode and the T-piece containing the liquid junction. The system has a constant diameter of 1 mm all the way through the capillary glass electrode and the T-piece. Gravity flow, a peristaltic pump or slight pressure from the groundwater sampling device was used to transport sample through the flow cell. During pH measurement of groundwaters, the flow cell was always directly coupled to the groundwater sampler, so that no degassing or air admission could occur.

The liquid junction is formed in the lower arm of the T-pieces, and is clearly visible as a sharp interface between the dilute sample and the dense KCL solution. The lower arm of the T-piece is connected to a reservoir filled with 3.5 M KCl containing the calomel reference electrode (Radiometer K104) and which is

completely closed except for a connection to a micrometer burette. All tubing is 1 mm bore PTFE. By displacing volume with the micrometer burette, the liquid junction in the T-piece can be renewed. The whole apparatus was build into a perspex box, which was thermostated by circulating water. The perspex box was enclosed in a Faraday cage and the whole apparatus was carefully earthed. pH was measured with a WTW PH 196 instrument.

Performance of the pH flow cell

In order to test the performance of the flow cell in the laboratory, the dilute buffer solutions described by Covington et al. (1983) were used. First the flow cell was calibrated with commercial Radiometer pH 4, 7 and 9 buffer solutions of high ionic strenght and subsequently the dilute Covington buffer solutions were measured. During each measurement, the liquid junction was renewed at least once to ensure that a reproducible liquid junction potential was established. The Nernstian slope of the measuring cell was found to be 58.4 mV per pH unit (25°C) which is close to the theoretical value of 59 mV (Davison, 1987).

TABLE 1. pH of diluted buffer solutions at 25°C: A, predicted by Covington et al. (1983) and B, measured with the flow cell.

Buffer Solution	Molality mol/kg	pH-A	pH-B
$KHC_8H_4O_7$	.01	4.117	4.08
Na_2HPO_4-KH_2PO_4 (1+1)	.0025-.0025	7.068	7.05
KH_2PO_4-Na_2HPO_4 (1+3.5)	.0008695-.003043	7.605	7.59

The results are shown in Table 1 and show that the values measured with the flow cell are within 0.02 pH unit from the values listed by Covington (1983). On this background, we concluded that the flow cell performs satisfactory under laboratory conditions.

Performance under field conditions was. however, frauded with a number of problems. These include first of all problems with static electricity, and controlling flow rates and pressure differences within the system. The latter were solved by installing a pressure alignment between the KCl reservoir and the outlet of the T-piece. Problems with static eletricity appear difficult to control and have also been described by Harbinson and Davison (1987). In addition, gas bubble formation within the capillary of the flow cell, due to degassing of the groundwater sample, often occurred. Such gas bubbles could disturb both the glas electrode capillary and the liquid junction, and result in unstable potentials.

Typical results for pH measured as a function of sample volume retrieved (equaling time) from the groundwater sampler are shown in Fig. 3. Generally the signal appears to be stable to about ± 0.1 pH unit. Larger variations in the potential are probably due to small bubbles passing the flow cell as mentioned before. The slight increase in pH towards the end of the sample volume, probably reflects a real change in pH.

Our next step was to compare the pH values measured in the field with our standard method, with those carried out using the flow cell. The two sets of measurements were carried out on different batches of groundwater retrieved from the sampler, but other data suggests that no major changes between batches are to

be expected. The results of the comparison are displayed in Fig. 4. There is a reasonable agreement between the two sets of data over the pH range 4.5 to 8, but also a fair amount of scatter. However, no systematic differences between the two sets of data seem to be present.

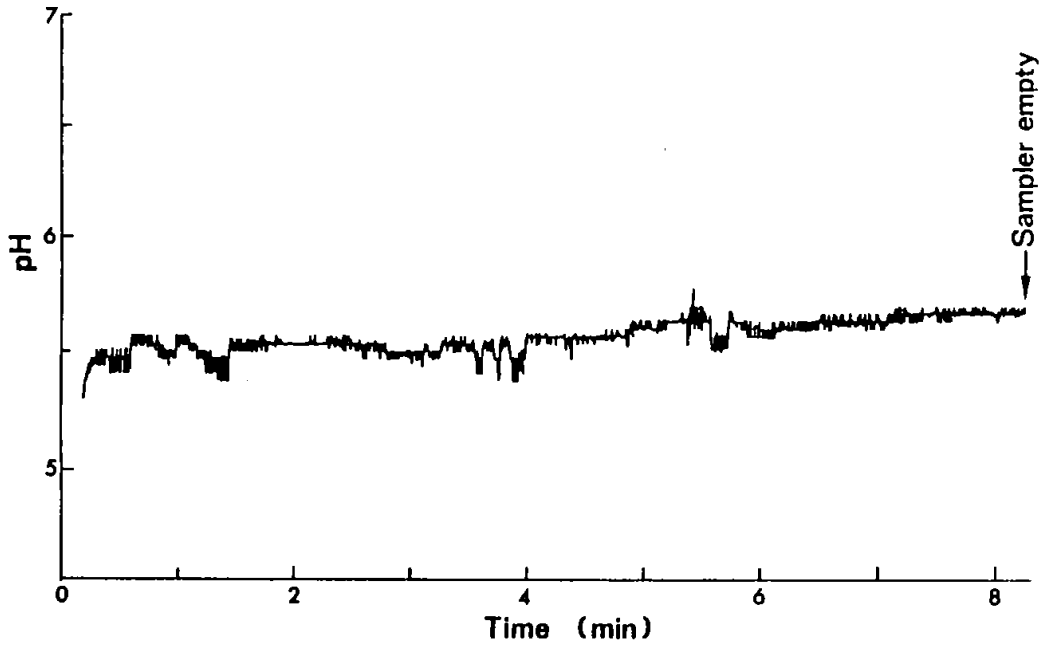

FIG. 3 pH in groundwater, measured with the flow cell, as a function of the volume sample recovered (= time) from a double line gas driven sampling device.

At this stage our dilemma became which data set should be preferred. Theoretically, the data from the flow cell should be the most reliable as far as liquid junction problems concerned. However, the rather unstable behavior of the flow cell in the field, required additional documentation of it correct performance. There seems to be no rigeous test available for determining the

correct in situ pH of the groundwater samples. However, a check for internal consistency can be obtained by calculating pH from Total Inorganic Carbon (TIC) and alkalinity, which both can be analysed with high precision. Such calculations include ion activity corrections and ion complexing based on knowledge of all major ion concentrations. The calculations were carried out with the computer program WATEQP, developed by Tony Appelo, Free University of Amsterdam. WATEQP is a Turbo Pascal version of WATEQF (Plummer et al., 1976) with additional options for pH calculation from

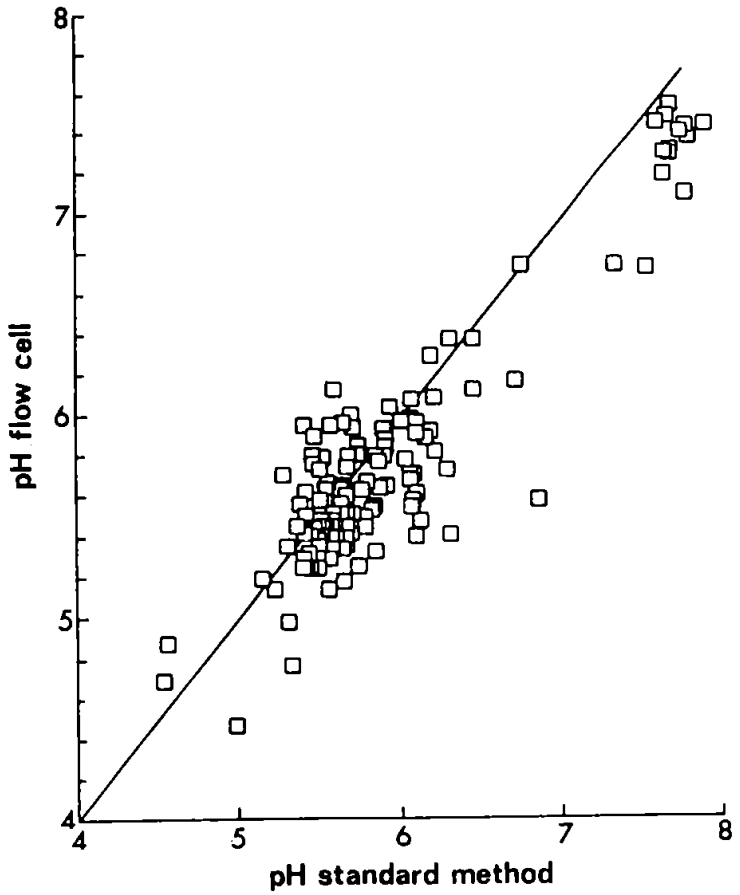

FIG. 4 A comparison of pH values measured by the standard open vessel method and the flow cell in poorly buffered groundwaters near Rabis Bæk, Denmark.

other parameters in the carbonate system. The thermodynamic data base of WATEQP is for the CO_2-H_2O-$CaCO_3$ system based on the consistent set compiled by Plummer and Busenberg (1982). The results of calculated pH values together with results of field pH measurements, obtained by the two different methods are shown in Fig. 5. Very good agreement is found between the pH measurements carried out with the standard method and the calculated values. The agreement is generally within 0.1 pH unit. This is particularly good considering the fact that they represent different batches of groundwater retrieved from the multisampler. There are, however, major deviations between calculated pH values and those measured with the new flow cell. Flow cell measurements are in most cases significantly higher than calculated pH values and this could indicate that degassing within the capillary glass electrode is a problem.

Although the disagreement between calculated pH values and those measured with the flow cell does not prove that flow cell values are incorrect, we feel considering the number of problems with the use of the flow cell in the field, that the flow cell pH values are not acceptable at present. Apparently, further development is needed to make the flow cell perform satisfactory in the field. These include both a solution for the static electricity problems, as well as avoiding the decrease from **in situ** to surface pressure, previous to the measurements.

On the other hand, the consistency between alkalinity, TIC and pH measured by standard procedures gives us a high level of confidence in our standard procedures.

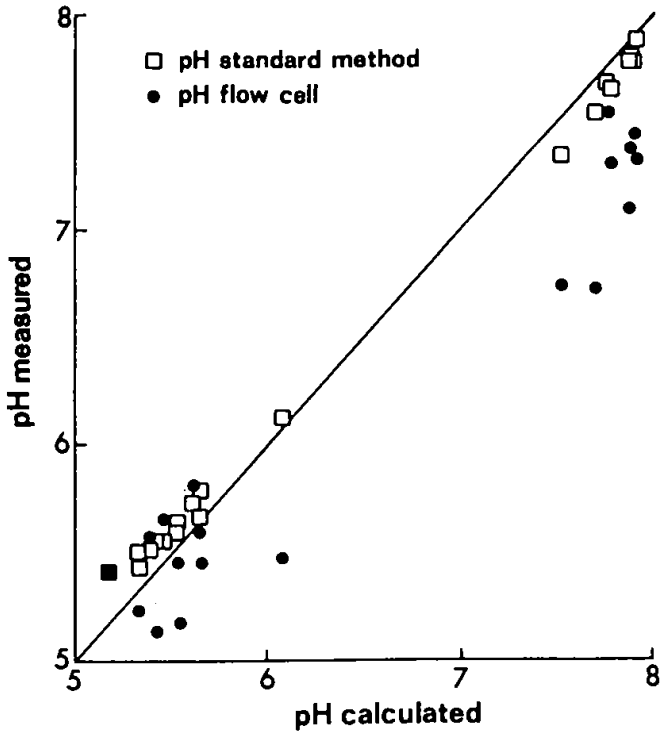

FIG. 5 A comparison of pH measured with two different techniques and pH values calculated from alkalinity and TIC.

CONCLUSIONS

The results of this study show that careful field pH measurements are absolutely necessary in order to obtain reliable values. In that case, it is possible to obtain a consistent data set including pH, alkalinity and TIC.

A new developed flow cell, based on a capillary glass electrode and a T-piece type renewable free-diffusion liquid junction worked well in the laboratory but is at the present stage still unreliable for field use. Problems with static electricity and degassing of the sample remain difficult to overcome.

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APPENDIX A3

GUIDELINES FOR FIELD ANALYSIS OF SOME REDOX SENSITIVE COMPONENTS IN GROUNDWATERS

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INTRODUCTION

Reliable information concerning redox components in ground waters is of utmost importance for obtaining a good understanding of geochemical redox processes occuring in aquifers. For obtaining such high quality data, special care should be taken with methods of groundwater sampling, sample retrieval, and field analysis. It is not recommended to follow any universal procedure in such matters. In each separate case, the methods should be evaluated carefully and the critical parameters identified, depending of the purpose of the study and the processes occurring in the aquifer. Too many procedures carried out in the field, often under poor conditions, tend to lower the quality of the data collected and is very costly as well.

A prerequisite for any field analysis is that groundwater sampling is carried out depth specific and without any contact with the atmosphere. Mixed waters, for example containing both oxygen and high Fe^{2+}, are impossible to deal with analytically. Anoxic sampling and filtration procedures for groundwaters are discussed elsewhere in this report. Preferable, 0.1 μm filters should be used (Kennedy and Zellweger, 1974).

This paper is not a complete analytical field manual, it should rather be considered as a state of art report, collecting experiences which could be useful for other researchers. It contains discussions and descriptions of measurements of oxygen, pH, ferrous iron, hydrogen sulfide and some comments on nitrite and phosphate. Eh measurements are not included, since they are only useful as qualitative indicaters. Make those as sloppy as possible, so you will not be tempted to relate them to anything

quantitative afterwards. Many workers before have wasted a lot of time on such illusions.

Field equipment should, apart from pH and O_2 meters, filtration equipment etc., include a good battery driven spectrophotometer. At present, the best available instrument seems to be Dr Lange LP 1W. It compensates automatically for power fluctuations, has good optics, and is delivered with interference filters. Last but not least, some protection from the weather should be available, rain as well as sun. We used a laboratory equiped van from the Geological Survey of Denmark.

FERROUS IRON

Ferrous iron may occur in anoxic groundwaters at concentrations of more than 1 mMole/l at pH 6. Since the oxidation rate of Fe^{2+} at pH 5-7 is extremely fast; at pH 7 and in contact with the atmosphere the half-time for Fe^{2+} oxidation is 4 minutes (Theis and Singer, 1973). Thus there is a major risk for loss of Fe^{2+} during sampling handling, filtration and analysis. Troup et al. (1974), showed that adsorption of O_2 on membrane filters may produce a significant losses of Fe^{2+}.

Analytically, there are two approaches towards obtaining proper Fe^{2+} results. In the first approach, it is considered that Fe^{3+} becomes very insoluble at pH values higher than 5. It is assumed then that all Fe which passes through a certain filter size, like 0.45 or 0.1 μm, is in the ferrous state. The filtered sample is acidified and total Fe is measured back in the laboratory. Although 0.1 μm filters are a better choice, several workers (Kennedy and Zellweger, 1974; Laxen and Chandler, 1983)

have showed that some of the suspended iron has particle sizes of less than 0.1 μm. Furthermore, there exists a risk that Fe^{2+} which is firmly complexed by organic matter is included as free Fe^{2+}. Also Shapiro (1966) showed that ferric iron in acidified humic samples may reduce to ferrous iron. In any case, the filtration approach will work best in fully reduced environments, where no fine grained iron oxyhydroxides are present.

Alternatively, Fe^{2+} can be measured in the field, immediately after sample retrieval, using colorimetrical methods and a field spectrophotometer. Colorimetric methods are all based on a specific coloured complex between Fe^{2+} and a organic ligand and commonly used methods are bathophenanthroline (Lee and Stumm, 1960), 2,2'bipiridyl (Rainwater and Thatcher, 1960; Heaney and Davison, 1977) and ferrozine (Stookey, 1970; Gibbs, 1979). A discussion of different methods can be found in Eichelsdörfer and Rosopulo (1968). Heaney and Davison (1977) compared the 2.2'bipiridyl method with polarography in water containing both ferrous and ferric iron. When samples are protected from strong solar irradiation, air contact, and measurements are made quickly, the 2.2'bipiridyl method was found to be specific for ferrous iron. The same is no doubt valid for the two other methods. Immediate measurement is required to avoid slowly increasing absorbances due to Fe^{2+} release from organic complexes or displaced Fe^{2+}/Fe^{3+} ratios (Heaney and Davison, 1977). Strong solar irradiation may cause photoreduction of ferric compounds (Lee and Stumm, 1960). The main advantage of the ferrozine method, which presently is most in use, is the somewhat higher sensitivity. We have used the 2,2'bipiridyl method in cases were high Fe^{2+} concentrations are expected, such as at

the site of pyrite oxidation, while with low Fe^{2+} contents, as in many groundwaters, the ferrozine method is preferred.

Procedure for Fe^{2+} determination with ferrozine

General

Fe2+ forms with ferrozine instantaneously a magnenta coloured complex which can be measured spectrophotometrically at 562 nm. The colour intensity of the complex is stable in the pH range 4 to 10, however, the use of a 5.6 buffer is recommended for general purposes. The analysis should be carried out immediately after anoxic sample retrieval and filtration. The procedure described here is a micro version, routinely used for groundwaters and porewaters.

Equipment

A battery driven field spectrophotometer with a 562 nm filter. Eppendorf pipettes, disposable 1 cm cuvettes and 12 ml disposable plastic vials.

Reagents

Ferrozine solution: 0.257 g Ferrozine (3-/2-pyridyl)-5,6-bis/4-phenyl sulfonic acid)-1,2,4 triazine; di-Na-salt) is dissolved in 50 ml H_2O.

Na-acetate buffer solution: 350 g CH_3COONa is dissolved in 1 liter dest. H_2O. The solution is adjusted to pH 5.6 with HCl.

Procedure

Pipette 0.1 ml ferrozine into 12 ml vials. Add a aliquot of

sample, taking care that the sample is injected directly into the ferrozine, so that immediate complexation is accomplished. Then add 0.1 ml buffer solution and dilute to a total volume of 5 ml. The absorbance is read immediately on the spectrophotometer.

It is important that the order of addition is done as described. Any reversal, like pipetting sample in the vial before ferrozine addition or dilution of the sample from the start may cause serious losses of Fe^{2+}, even when deoxygenated reagents are used.

With the procedure described, the detection limit routinely attained is about 50 µg/l and the Beer-Lambert law is obeyed to at least 3 mg/l, corresponding to an absorbance of about 1.5.
An alternative procedure which can be of use is add ferrozine to a measuring glass, then drain sample directly into the ferrozine until proper colour has developed. Then read the amount of sample added, add buffer and dilute to the total volume. Care should here be taken that the volume of the sample is not too small compared to the total volume of the measuring glass, since this will give uncertain sample volumes.

Interferences are known for divalent cobolt, monovalent cobber, nickel, high oxalate, cyanide, nitrite and high hydrogen sulfide concentrations. However, in practice, these are in most cases of minor importance.

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HYDROGEN SULFIDE

Analyses of H_2S are subject to severe errors due to degassing as well as oxidation. Precautions include immediate fixation and/or immediate analysis in the field. A number of techniques are available for analysis of dissolved sulfide. These include iodometric titration (A.P.H.A., 1975), the use of a Ag-AgS_2 membrane electrode combined with Hg^{2+} titration (Boulègue et al., 1979), polarography (Luther et al., 1985), and spectrophotometry (Cline, 1969). Particularly the latter method is very suitable for field analysis.

Procedure for dissolved sulfide analysis with methylene blue

General

Dissolved sulfide reacts with N,N-dimethyl-p-phenylendiamin-sulfat and Fe^{3+} under production of methylene blue. The color intensity of the latter is proportional to the dissolved sulfide concentration.

Particular care should be taken to avoid degassing and oxidation. In the original description of Cline (1969) different reagents are used for three different concentration ranges, which then are measured directly. We prefer only to use the lower range reagent and dilute Zn-acetate suspensions if necessary. The micro version described here is suitable for groundwaters and porewaters.

Equipment

A battery driven field spectrophotometer with a 670 nm filter. Eppendorf pipettes, disposable 1 cm cuvettes and 10 ml measuring glasses.

Reagents

Mixed diamine reagent: Dissolve 2.0 g diamine and 3.0 g $FeCl_3 \cdot 6H_2O$ in 500 ml **cold** (< 10°C) 50% (v/v) HCl. The reagent is stable for a couple of months when stored refrigerated in a dark bottle.

Zn-acetate solution: Dissolve 40 g $Zn(CH_3COO)_2$ in one liter H_2O.

Standardization: Calibration curves are usually prepared from $Na_2S \cdot 9H_2O$ standard solutions. These are difficult to prepare anoxically. A good trick is to wash and dry the $Na_2S \cdot 9H_2O$ crystals, then drop them in a ten times diluted Zn-acetate solution, and wait until the crystals have completely dissolved. Then homogenize with a Vortex mixer and use the ZnS suspension as standard solution.

Procedure

Pipette 1 ml Zn-acetate solution in 10 ml measuring glasses. Ensure that sampling and filtration occur without degassing or air contact. **Immerse the drain from the filtration unit below the Zn-acetate surface in the measuring glass.** Collect sample until ZnS precipitate becomes visible, but use at least 5 ml sample. Read the sample volume and fill the remainder up to the 10 ml mark with ten times diluted Zn-acetate solution. Homogenize and add 0.8 ml mixed diamine reagent. Wait 20 minutes and measure the absorbance at 670 nm. ZnS suspensions which are too strong can be diluted, after vigorous shaking, into diluted Zn-acetate solutions. In that case also more Zn-acetate can be used in the initial step.

The detection limit routinely obtained is 0.1 mg/l H_2S and Beer-Lambert law is obeyed to at least 1 mg/l H_2S. Some workers bring samples conserved with Zn-acetate back to the laboratory for H_2S

measurement. In that case the samples should be stored cool and dark and be measured within one week. If a field spectrophotometer is available, field measurement seems preferable.

Interferences

The presence of thiosulfate may inhibit color development (Cline, 1969). Also in the presence of polysulfide, the concentration of total dissolved sulfide seems to be underestimated (Luther et al., 1985).

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ALKALINITY

Titration alkalinity is a measure for the acid neutralizing capacity of a groundwater sample. In practice it is used to determine the amount of dissociated carbonic acid in solution. A simple definition, suitable for most purposes is:

Alkalinity = $m_{HCO3^-} + 2 \cdot m_{CO3^{2-}}$

Actually, all other dissolved species which might accept a proton should be considered, such as dissolved sulfides, phosphates, complexes, organic acids and also OH^- when starting from high pH. The contribution of such species can be calculated with computer speciation programs like WATEQF, but are in most cases small.

Sources of errors in alkalinity detrminations are $CaCO_3$ precipitation, due to CO_2 degassing, precipitation of iron oxyhydroxides, oxidation of dissolved sulfide etc. Therefore, alkalinity determinations should be made in the field as quickly as possible.

Traditionally, alkalinity is determined by titration with HCl down to pH 4.5. However, problems with overshooting the end point, etc makes it a tedious method for field use. A much more precise and fool proof method is the use of GRAN titration (Stumm and Morgan, 1981; Gieskes and Rogers, 1973). The principle of the GRAN titration is to monitor the $[H^+]$ increase with volume titrant, past the equivalent point and then extrapolate backwards to the equivalent point. This is illustrated in Fig. 1

Main advantages of GRAN titrations are; a) problems with precipitation can be avoided since the sample is titrated quickly down below pH 5, b) Precise calibration of pH electrodes is not

important, c) the equivalent point is obtained by linear regression from at least 5 pH readings.

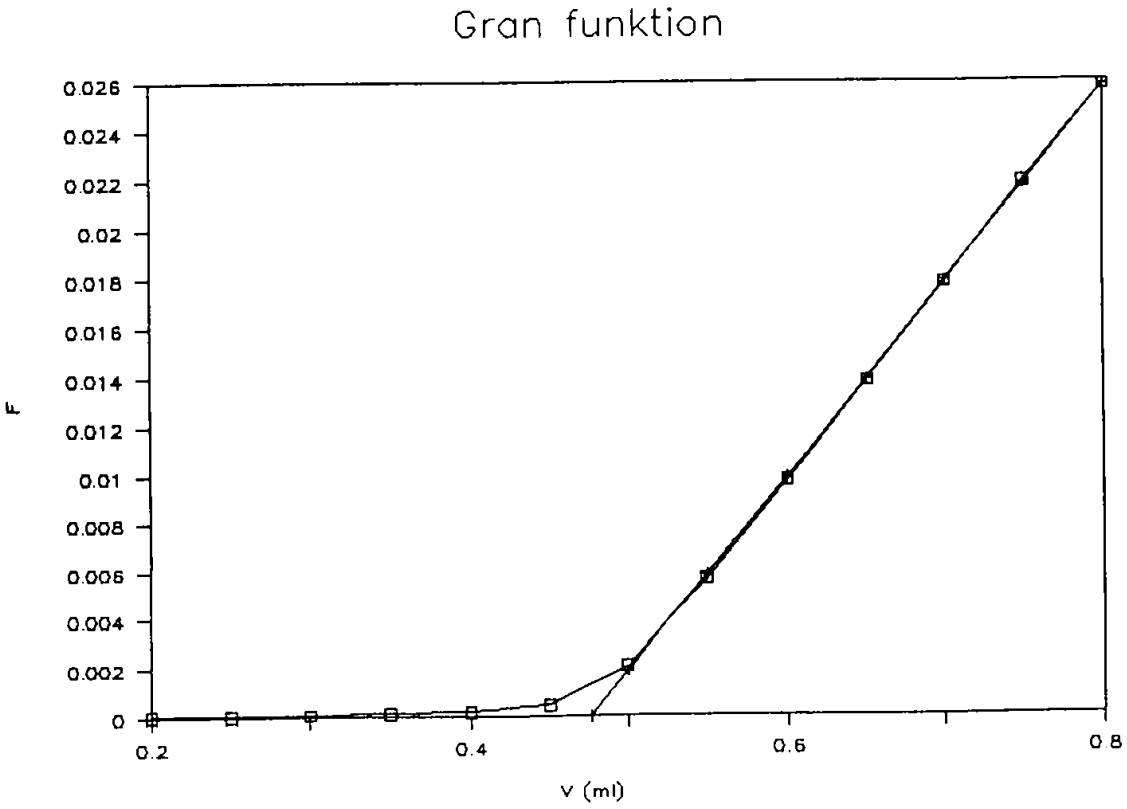

FIG. 1. A GRAN plot for alkalinity determination, showing ml titrant versus the GRAN function F. The equivalent point is found by extrapolation of the linear part to F = 0.

Procedure for alkalinity determination with GRAN titration

General

The sample is titrated with dilute HCl while monitoring the change in pH. In order to avoid precipitation and oxidation, the titration should be carried out immediately after sample retrieval. For the same reasons, the sample should be titrated quickly to just below pH 5. Then small constant volumes of acid are added and

the pH is recorded after each addition until pH 3 is reached.

From the recorded data, the GRAN function F is calculated:

$$F = (V + V_o) \cdot 10^{-pH}$$

where V_o = the original sample volume

V = the added volume of acid

A plot of F versus ml acid added should show a linear relationship past the equivalent point. This is extrapolated to F = 0 and gives the ml of acid corresponding to the equivalent point. To facilitate these calculations a macro was written by Jacob Egede which performs these calculations by use of a LOTUS spreadsheet program and also shows graphically the resulting plot. If the GRAN plot is not linear, a quantitative important weak acid or high dissolved Al might be present and further checks should be made to identify the problem. In that case a pH measurement combined with TIC might be more suitable to describe the dissolved carbonate systems.

Equipment

A 5 ml piston burette, for example available from Metrohm, with a standardized HCl solution with a strenght ranging from 0.1 N to 0.05 N depending on sample size and alkalinity.

Furthermore, a calibrated pH meter with electrodes, a battery driven magnetic stirrer, and a titration vessel, for example disposable 50 ml plastic vials.

Procedure

Pipette 25 ml of filtrated sample into the titration vessel immediately after sample recovery. Immerse pH electrodes and a magnetic stirrer bar and titrate quickly down to just below pH 5. Read pH and volume HCl used precisely and start adding small

constant amounts of HCl, for example 0.05 ml. Read stable pH values after each addition and proceed down to pH 3.

The calculation of the alkalinity is done most easy with the enclosed LOTUS macro. Retrieve the GRAN.WK1 spreadsheet file, press Alt-M and the menu leads you through the calculations.

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PH MEASUREMENT

The measurement of pH in natural waters is at the same time the easiest and most difficult field procedure. The easiest because you simply immerse a calibrated combined glass electrode in the sample and wait for a stable reading. The most difficult because thermodynamical meaningful measurements, particularly in poorly buffered systems, require great care and a number of precautions. The definition of pH is simply:

$$pH = -\text{Log } a_{H^+}$$

As such it is used directly in speciation and saturation calculations with computer programs like WATEQF. Since it is a logarithmic unit, small pH errors will have large effects on such calculations. Interlaboratory comparison of pH measurements in the field using poorly buffered river water showed total errors in excess of 0.2 pH unit (Davison and Gardner, 1986). Errors comprise liquid junction problems, humidity problems with electronic equipment, calibration problems etc.

Still, pH of most groundwater samples are liable to changes due to degassing of particularly CO_2, precipitation and oxidation etc. Therefore, immediately field analysis remains the preferred procedure. Some workers use flow cells, while others, measure pH in open vessels. Although flow cells, might reduce the risk of degassing, great care should be taken to avoid pressure to build up in the flow cell. This would obstruct the free and constant seepage of electrolyte from the reference electrode, creating highly irreproducible liquid junctions, which might seriously affect the measurements. The problems and uncertainties involved

in pH measurements are elaborated upon elsewhere in this report.

At present, there is no procedure that can guarantee correct pH values. However, the procedure described here has shown to produce results which are consistent with pH values calculated from concurrent measurements of alkalinity and total inorganic carbon by the aid of the speciation program WATEQP.

Procedure for field pH measurement

General

In a pH measurement, the activity of the H^+ ion is measured with H^+-sensitive glass electrode against the known potential of a reference electrode, in most cases a saturated calomel electrode. Both electrodes are often build together in one combination electrode. Electrochemical details concerning pH measurements can be found in Bates (1973).

Equipment

A good quality field pH meter, we use a WTW pH196 instrument. Also a combination electrode (our choice is Radiometer GK 2401C). Buffer solutions embracing the pH range that cover the sample range, and for which the temperature dependency is known. We use ready made Radiometer 4.01, 7.00 and 9.18 buffer solutions.

Procedure

Make sure that the electrode is free of air bubbles and fill the electrode completely with saturated KCl. Keep the filling port open also during overnight storage. Refill regularly when the KCl level drops to ensure contineous electrolyte leakage. Preferable

soak the electrode overnight before use in a pH 4 buffer solution with a open KCl filling port.

Bring buffer solutions and the electrode to groundwater temperature in a water bassin replenished regularly from the boring. Make a two buffer calibration starting with pH 7, while rinsing carefully with distilled water in between. Using the WTW instrument, this is a automatic press button operation, which furthermore yields details on electrode performance, like Nernstian slope. These should be recorded daily in order to monitor any electrode deterioration. With other instruments, the buffer knob is used for the pH 7 buffer and the Temp. knob for the second buffer. Note that calibrating the electrode at higher temperature, followed by adjustment with the Temp. knob to groundwater temperature gives incorrect results.

Recheck both buffer solutions; measurements should be made in quiescent solutions. Rinse carefully and immerse the electrode in the solution to be measured. Stir gently and let the solution come to rest. In low poised samples, stabilization may take several minutes. Take a new batch of sample and remeasure pH, it should give the same result. Finally recheck both buffer solutions. Place the electrode in the pH 4 buffer solution when not in use.

Electrode performance tests

The following electrode performance tests suggested by Davison (1987) would be useful to carry out regularly.

1) Electrode sensitivity; Using the standard calibration buffers and the pH meter in mV mode, verify that the electrode gives a Nernstian response: at 20°C, 58±1 mV per pH unit and at 25°

C, 59±1 mV per pH unit.

2) Accuracy in dilute solutions: Prepare accurately by weight, from commercial volumetric stock, a solution of 10^{-4} M HCl. The pH of this solution should be 4.00±0.02, irrespectively of wether the solution is stirred or quiescent. If the pH of the acid is outside these limits, dilute accurately, by 5 fold, a solution of pH 4.00 buffer. At 20°C, the pH should be 4.11±0.01, at 25°C 4.12±0.01. If these values are obtained on stirred and unstirred solutions, the preparation of the acid is probably in error.

3) Stirring shift; The shift in pH upon stirring a formerly quiescent solution of the acid should be <0.02 pH.

4) Response time; The reading obtained using dilute acid should be stable to within 0.01 pH unit, within 2 min of immersion of the electrodes, irrespective of the solution used prior to washing.

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OXYGEN

Oxygen contents of ground waters may range from close to atmospheric contents to completely anoxic conditions. Thus the prime source of error is gas exchange between the atmosphere and the sample, and this requires special care during sampling.

The classical method for dissolved oxygen analysis is the Winkler titration. Here O_2 is fixed as Mn-oxide which afterwards is titrated iodometrically. In recent years also the O_2 electrode has become popular. It is based on a polarographic reduction of O_2 at a silver electrode. The flux of O_2 across a plastic membrane placed in front of the electrode is proportional to the oxygen concentration in the sample. A weak point in the Winkler method, is the rather complex procedure which always involve a risk of atmospheric contamination. Furthermore interferences are known for NO_2^-, Fe^{2+}, Fe^{3+}, H_2S and dissolved organic matter. Special procedures to avoid such interferences are described in A.P.H.A. (1975). The electrode method is free for interferences except for other gasses, such as H_2S, which also diffuse through the plastic membrane. Thus when the electrode has been used in anoxic waters, frequent calibrations should be made. At low O_2 levels (< 1 ppm) electrode measurements seem to become unreliable (see elswhere in this report) and the Winkler method is apparently superior in this range. We have made a comparison of the Winkler and electrode methods for groundwaters under field conditions (FIG. 2). Generally good agreement is found, although results obtained with the Winkler method are slightly higher. This might reflect problems with sample collection without atmospheric contamination.

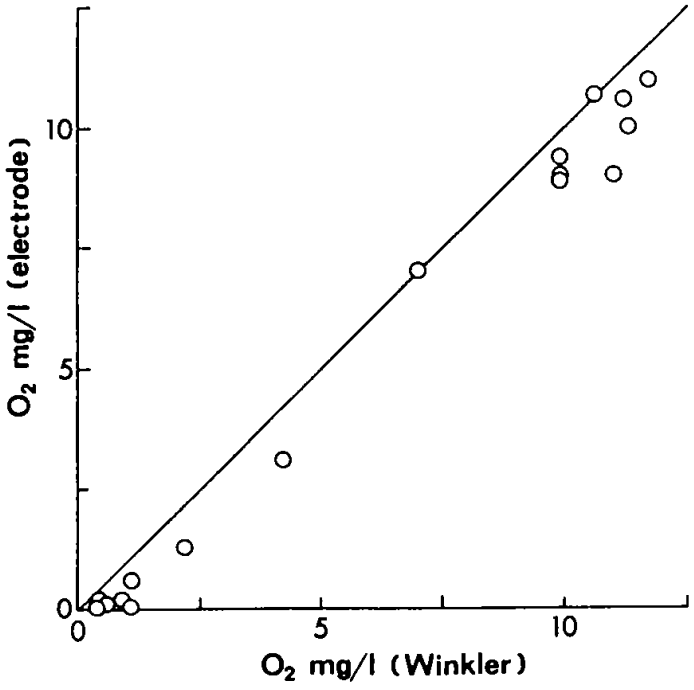

FIG. 2. Comparison of the Winkler and electrode method for determination of O_2 in groundwater sampled with a double line gas driven device.

The real problem with O_2 measurements in groundwaters, is apparently not to be the analytical method used, but rather sample retrieval problems. If suction is used, there is a obvious risk for degassing. But also if double line gas driven sampling devices are used, there is a risk of gas exchange between the sample and the drive gas used during transport of the sample to the surface. The latter case is illustrated in FIG. 3 where the measured O_2 content is displayed as a function of the amount of sample

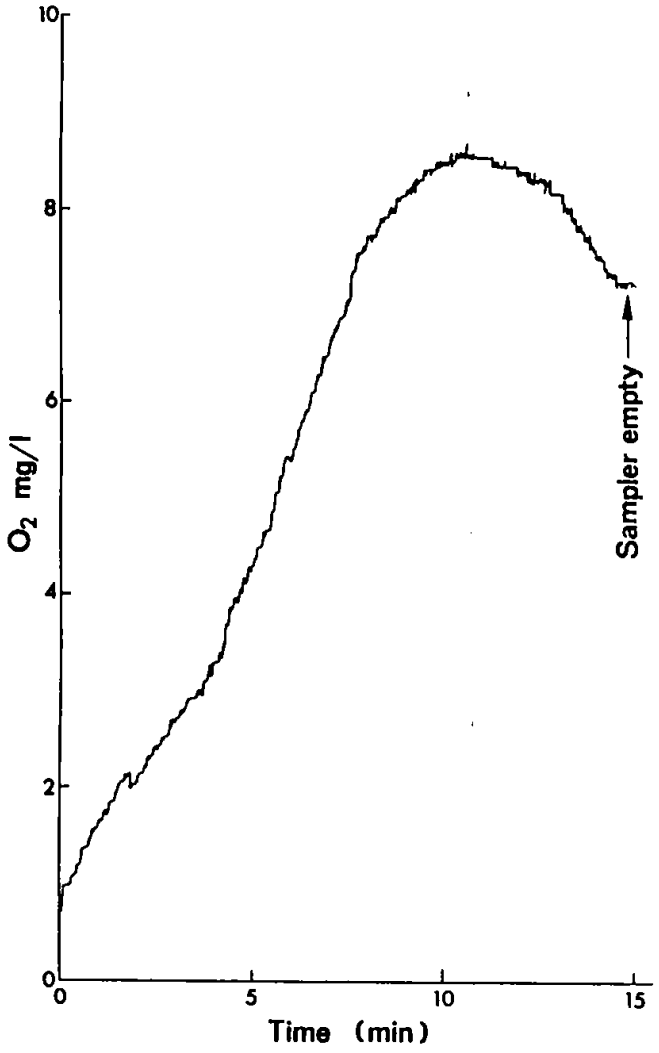

FIG. 3. The change in oxygen concentration as a function of the retrieved sample volume, corresponding to time. The sample was taken from a 22 m deep level, reflecting oxygen rich waters in a sandy aquifer.

recovered. Here a O_2-rich sample is retrieved using N_2 as drive gas from 22 m below the surface. Emptying the sampler several times before the sample is retrieved has filled the whole system with N_2. The increase in O_2 at the start, and decrease in the terminal part apparently reflects gas exchange at the gas water

interface in both tubings. Obviously the O_2 content should be monitored contineously to ensure that a correct measurement is made. Perhaps downhole operated syringe pumps (Gillham and Johnson, 1981) are more reliable for gas sampling of groundwaters.

Procedure for O_2 determination by electrode

General

Dissolved oxygen is measured with a polarographic probe with built-in thermistor for temperature measurement. The probe is covered with a plastic membrane. The electrode removes the oxygen behind the membrane and the flux of O_2 from the sample through the membrane is proportional to the oxygen content of the sample.

To avoid atmospheric contamination the probe is placed in a flow cell coupled on line to the sampler. Since the probe consumes O_2, a contineous fresh supply of sample should be ensured either by sample flow or by stirring.

Equipment

A WTW OXI196 oxygen meter with a WTW EO196-1.5 O_2- probe. Furthermore a flow cell (WTW D200) with a stirring bar and a battery driven magnetic stirrer. Preferable the signal of the instrument should be monitored contineously with a recorder.

Procedure

Make sure that the electrolyte below the membrane of the electrode is free of air bubbles. If the electrode has been out of use for a longer period, it should be polarized for about one hour. For pauses of less than one hour, the polarization time can be reduced

to about 20 min. A one-point calibration is made using the calibration tube, containing a H_2O wetted sponge, corresponding to atmospheric O_2 saturation. An additional zero check can be carried out by measuring O_2 in distilled water freed for O_2 by N_2 bubbling.

During measurements, the electrode consumes O_2 and vigorous stirring and a reasonable large sample are therefore important. The use of a flow cell is recommended to avoid atmospheric O_2 contamination; flow rates should be in the range 300-1000 ml/min. Below 300ml/min a stirring device should be used. Take care that no gas bubbles are trapped below the electrode! For samples containing more than 3 $^{o}/oo$ salinity corrections should be applied.

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PHOSPHATE AND NITRITE ANALYSIS

Nitrite and phosphate subsamples are usually preserved for later analysis back in the laboratory. However, in studies where these components are particularly important, some special precautions should be taken.

Nitrite subsamples are usually preserved with a bactericide like $HgCl_2$ or thymol. However, at least at pH values below 6, nitrite may also selfdecompose inorganically (van Cleemput and Baert, 1978). There is a additional risk for reaction between Fe^{2+} and nitrite particularly at pH 8 (van Cleemput and Baert; 1983; Thorling et al., 1990). Since bactericides will not prevent inorganic reactions, it might be a better option, to carry nitrite analysis out in the field with the conventional spectrophotometric method.

Phosphate analysis in anoxic ground water can be jeopardized by filtration under oxic conditions. Adsorbed O_2 may result in iron oxyhydroxide precipitation on the membrane filter, which in turn may cause serious losses of phosphate by sorption (Bray et al., 1973). On the other hand acidification of the sample may cayse hydrolysis of organic phosphate compounds. There is a considerable litterature on different fractions of dissolved phosphate, which has been reviewed by Burton (1973). For work where phosphate concentrations are critical, it seems best to carry out field analysis under anoxic sample collection and filtration, using the standard molybdate blue method.

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APPENDIX A4

INTERLABORATORY COMPARISON OF FIELD TECHNIQUES FOR REDOX SENSITIVE COMPONENTS IN GROUNDWATERS

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INTRODUCTION

There exists general agreement upon the necessity of analysing groundwaters for redox sensitive components in the field (e.g. Garner, 1988). However, it remains difficult to validate the quality of such field data. Results will be affected by a number of difficult controlable factors such as sampling techniques, sample handling and filtration after recovery, but also by more diffuse influences like weather conditions during sampling. Therefore, it is in most cases next to impossible to verify rigeously the results obtained in the field with laboratory techniques. In two of the main environmental programs presently carried out in Denmark, the Landfill project and the NPO project, field analyses form a integral part of the data collection scheme. Since the two programs are carried out by research teams from different institutions, using different procedures in the field, it was felt appropriate to make a comparison of the results obtained when working side by side. Although this approach does not yield a rigeous evaluation of the precision of the collected data, it does give a good estimate of the level of confidence for the analytical results. Therefore a joint field trip was organized to the research site of the Landfill project, near Vejen, Jutland, where field analysis of redox sensitive components was carried out along the pollution plume emanating from the landfill. Field analysis were planned for Fe2+, O_2, H_2S, pH and alkalinity. Unfortunately, no H_2S was detected, while nearly all samples were at a very low O_2 level.

In the following, the results obtained by the Dept. of Environmental Engineering are designated by the acronym LtH, while

the Applied Geology team is identified as ITG.

METHODS

Ferrous iron was determined spectrophotometrically (ITG) in the field with the ferrozine method, using a Dr Lange LP 1W battery driven spectrophotometer equipped with a 562 nm filter. LtH filtered samples in the field through 0.1 μm membrane filters under anoxic conditions. Samples were acidified and the total Fe content measured in the laboratory by AAS.

Oxygen was by both teams measured with a WTW OXI 196 meter, equipped with a EO 196-1.5 electrode. ITG used a commercial D 200 flow cell with magnetic stirring. LtH used a larger, homebuilt perspex flow cell with oxygen, pH and redox electrodes fitted through the top. Also this cell was magnetically stirred.

pH was by both teams measured with a automatic two buffer calibration instrument of WTW (pH 196) with a Radiometer GK 2401C combination electrode. ITG determined pH in a open vessel immediately after sample recovery. Measurements were done on quiescent solutions after gentle initial stirring. When a stable potential was attained, the measurement was repeated on a new subsample in order to ensure that a reproducible measurement was obtained. LtH used the same flow cell as for oxygen measurements loading the sample directly from the sampler into the flow cell, and measuring pH on stirred solutions.

Alkalinity was by both teams measured with GRAN titrations (Stumm and Morgan, 1981). ITG used 10 or 25 ml aliquots which were titrated with 0.1 N HCl with magnetic stirring. LtH used 20 ml aliquots and 0.06 N H_2SO_4.

RESULTS AND DISCUSSION

Samples were taken from drive point single depth piezometers. These were equipped with a contra valve near the inlet, and sampled by using pressured N_2. Each piezometer was emptied three times before sampling. The two field teams took alternate turns to the first sample recovered. Each carried out their normal field procedures completely independent from the other. The ground water chemistry ranged from highly organically polluted water, to water only slightly affected by pollution.

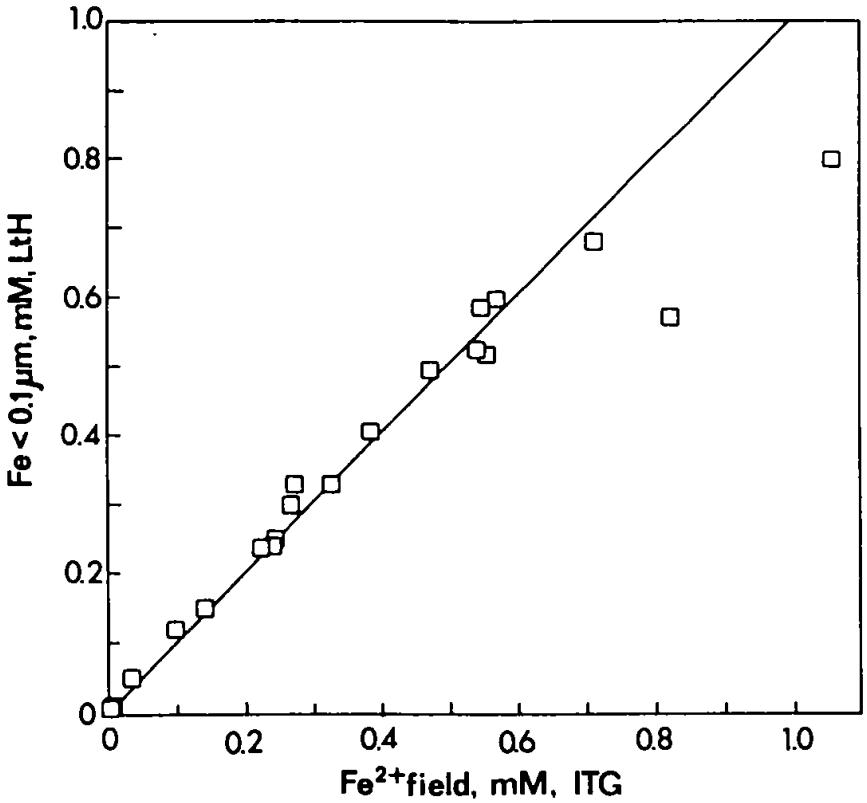

Fig. 1. Comparison of field analysis of Fe^{2+} by spectrophotometry and total Fe < 0.1 μm.

Ferrous iron determinations were carried out through a completely different approach by the two teams. The LtH team, filters samples anoxically through 0.1 μm membrane filters, and total iron which passes this filter is assumed to be present as ferrous iron. The ITG team measures Fe^{2+} specifically using a spectrophotometric method in the field. Comparison of the results is shown in Fig. 1, and shows generally a very good agreement. There appears to be no systematic disagreement over a wide range of ferrous iron concentration. A few outliers are present, were ITG values are significantly higher. There is no obvious explanation for the outliers, but possible sources of error are the large dilutions involved in both methods at high Fe concentrations.

However, generally the results for Fe^{2+} are fully satisfactory. Some caution is warranted in using the LtH method more in general, since in less reducing environments particular FeOOH can be present with a size of less than 0.1 μm (Kennedy and Zellweger, 1974; Laxen and Chandler, 1983).

Oxygen results are shown in Fig. 2 and are constricted by the low O_2 contents of ground waters at the field site. With one exception all results were less than 0.03 mM O_2 (< 1 ppm) and the agreement between the two sets of data is very bad. It is notable here that both teams used identical instruments and electrodes. The only difference was that the ITG team used a small commercial flow cell, while LtH used a larger volume flow cell constructed for simultaneous measurement of pH. The disagreement is clearly larger than the accuracy of 0.1 ppm, specified by the manufacturer in this range, but it is unclear whether the error is due to the actual measurement or to sample handling. A comparison between the

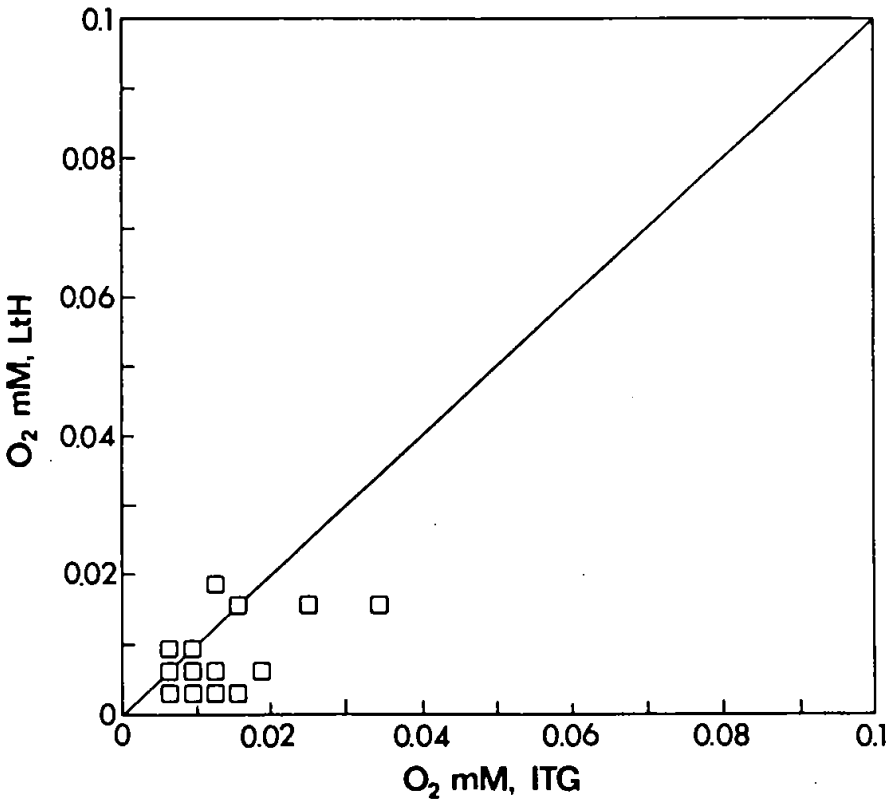

Fig. 2. Comparison of low level oxygen measurements made by electrode.

traditional Winkler method and the electrode method, reported elsewhere in this volume, applied to groundwaters has shown good general agreement, albeit over a much larger concentration range. At the present stage we are forced to conclude that low level (<0.03 mM) O_2 electrode measurements of groundwaters have little significance.

pH measurements are shown in Fig. 3. They display a reasonable general agreement, but still with a good deal of scatter in these fairly well buffered groundwaters. About 80 % of the data is within 0.25 pH unit from the one to one correlation, and this is comparable to the error of ± 0.2 pH reported for routine laboratory pH measurement of poorly buffered natural waters (Davison and

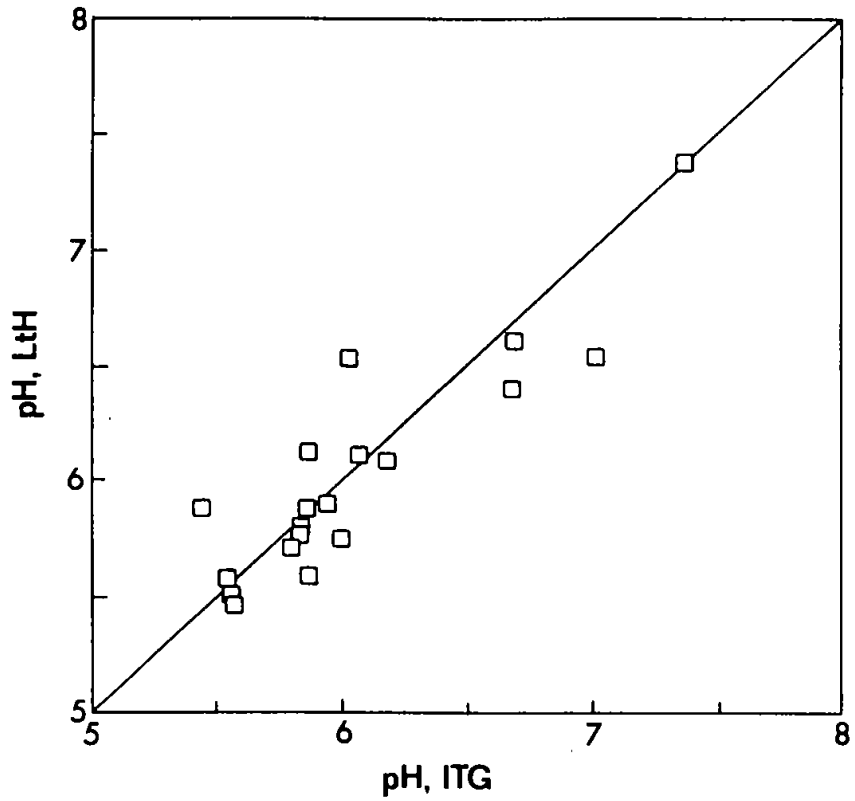

Fig. 3. Comparison of pH measurements made by flow cell (LtH) and open vessel with (ITG).

Gardner, 1986). According to these authors, field measurements are worse. The methods used by the two teams are slightly different; LtH used a flow cell which should minimize degassing, while ITG used an open vessel replenishment method. On the other hand, the ITG method was compared with pH values calculated from TIC and alkalinity using a speciation program, and here good agreement for low poised groundwaters was found. In any case Fig. 3 does not show any systematic deviations. Apparently, pH remains one of the most difficult parameters to measure accurately in groundwaters.

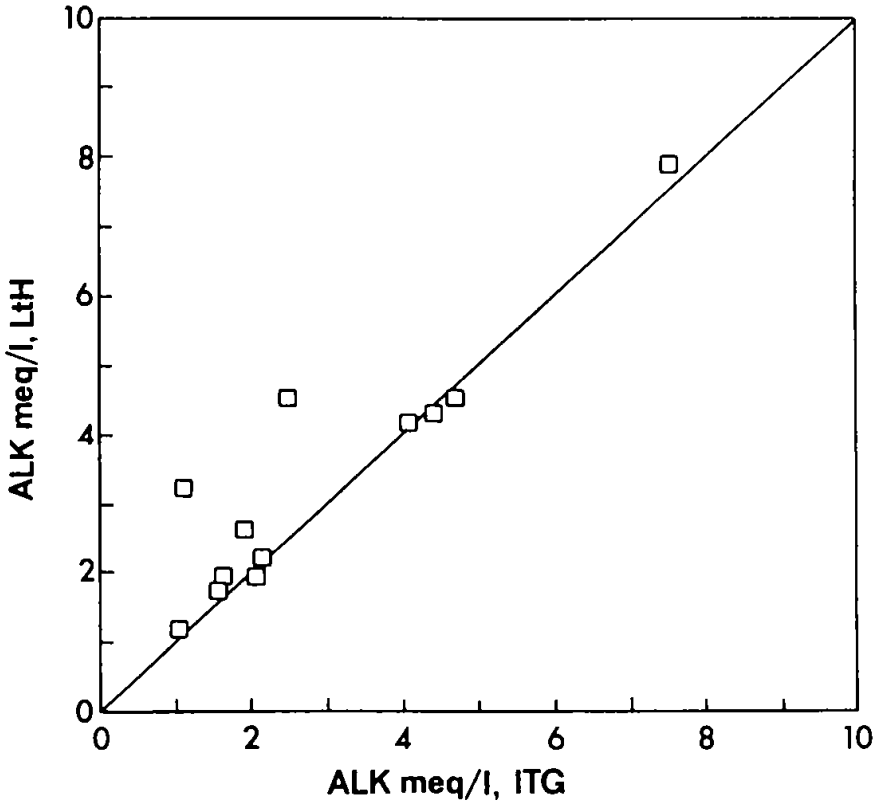

Fig. 4. Comparison of alkalinity measurements, carried out in both cases by GRAN titration.

Alkalinity results are shown in Fig. 4. Both teams used the GRAN titration which is one of the most fool proof field methods, since it does not depend on a single reading and is independent of any calibration error of glass electrodes. Therefore, a precision of about 1 to 2 % is to be expected. Results in Fig. 4 are also in good agreement for the two teams, but there are several outliers showing errors of more than 100 %. These deviations are unacceptable and also difficult to explain. Only miswriting titrated volumes may give errors of this magnitude.

CONCLUSION

This interlaboratoty comparison has shown reasonable general agreement between results obtained for Fe^{2+}, alkalinity and pH. However, low level O_2 measurements made by electrode show a close to random variation. For each parameter, outliers were found, which particularly in the case of alkalinity are unacceptable. These furthermore emphasize the need of continuous quality control on field analysis in order to ensure that they are also in reality more representative for in situ ground water chemistry than analyses performed back in the laboratory.

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